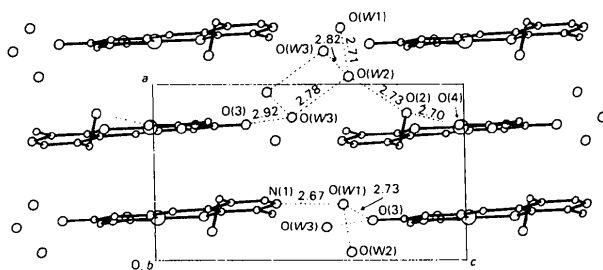


Fig. 1. The molecular structure.

Fig. 2. A view of the molecular packing parallel to *b*: only some hydrogen bonds are reported (dashed lines). (Distances in Å.)Table 3. *Hydrogen bonds*

| Donor | Acceptor | at | <i>D</i> ... <i>A</i> (Å) | <i>D</i> - <i>H</i> (Å) | <i>H</i> ... <i>A</i> (°) |
|-------|----------|-----------------------------------------|---------------------------|-------------------------|---------------------------|
| O(2) | O(4) | <i>x</i> , <i>y</i> +1, <i>z</i> | 2.701 (4) | 0.96 | 166 |
| N(1) | O(W1) | <i>x</i> , <i>y</i> , <i>z</i> +1 | 2.675 (5) | 0.98 | 162 |
| O(W1) | O(3) | <i>x</i> , <i>y</i> , <i>z</i> | 2.732 (4) | 0.91 | 176 |
| O(W1) | O(W2) | <i>x</i> , <i>y</i> , <i>z</i> | 2.712 (5) | 1.00 | 169 |
| O(W2) | O(2) | - <i>x</i> , 2- <i>y</i> , - <i>z</i> | 2.728 (4) | 0.87 | 163 |
| O(W2) | O(W3) | - <i>x</i> , 1- <i>y</i> , -1- <i>z</i> | 2.784 (5) | 0.93 | 170 |
| O(W3) | O(3) | <i>x</i> , <i>y</i> , <i>z</i> | 2.917 (5) | 1.08 | 168 |
| O(W3) | O(W2) | <i>x</i> , <i>y</i> -1, <i>z</i> | 2.823 (5) | 1.13 | 122 |

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The Structure of Bis(2,4-dinitrophenolato)tris(1,10-phenanthroline)barium(II), Ba(C₁₂H₈N₂)₃(C₆H₃N₂O₅)₂

BY J. A. KANTERS, R. POSTMA AND A. J. M. DUSENBERG

Structural Chemistry Group, Rijksuniversiteit Utrecht, Transitorium 3, Padualaan 8, 3508 TB Utrecht, The Netherlands

AND K. VENKATASUBRAMANIAN AND N. S. POONIA

Chemistry Department, University of Indore, Indore 452-001, India

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Abstract. $M_r = 1044.18$, monoclinic, $P2_1/n$, $a = 11.244$ (3), $b = 21.23$ (1), $c = 17.935$ (5) Å, $\beta = 93.42$ (3)°, $V = 4273$ (3) Å³, $Z = 4$, $D_m = 1.62$, $D_x = 1.62$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 9.16$ cm⁻¹, $F(000) = 2096$, $T = 294$ K, $R = 0.033$ for 5640 observed reflections. Ba is bonded to six N atoms of the three phenanthrolines (phen) and to the three O atoms of the dinitrophenolates (dnp), which form a mono-capped distorted square antiprismatic coordination. The N atoms of the three phen's are pair-wise ligated, the

fourth bidentate ligand is formed by phenolic and *o*-nitro-group O atoms of dnp1 and the coordination is completed by phenolic O of dnp2. The *o*-nitro group of dnp2 is disordered over two sites with occupancies of 0.55 and 0.45.

Introduction. In a previous paper we reported the structure of the acetone solvate of bis(1,10-phenanthroline)bis(2,4,6-trinitrophenolato)barium(II) (Postma, Kanters, Duseenberg, Venkatasubramanian &

Poonia, 1983) in which Ba is irregularly eightfold coordinated to the four N atoms of the phen's and four O atoms of the tnp's and acetone respectively. Now we report the structure of an analogous complex, bis(2,4-dinitrophenolato)tris(1,10-phenanthroline)barium(II).

Experimental. Yellow crystals prepared by dissolving barium dinitrophenolate in acetone-ethanol to which a twofold excess of 1,10-phenanthroline had been added. Rod-shaped crystal, $0.35 \times 0.20 \times 0.15$ mm, D_m by flotation, 7517 independent intensities in one quadrant of the reflection sphere ($2\theta_{\text{max}} = 50^\circ$), Nonius CAD-4 diffractometer, Zn-filtered $\text{Mo K}\alpha$, ω - 2θ scan, 5640 above $2.5 \sigma(I)$ level; lattice parameters refined by a least-squares procedure utilising 24 reflections; one periodically measured standard reflection showed insignificant changes during data collection; corrections not applied for absorption; structure solved with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and subsequent Fourier methods; all H atoms located from difference syntheses, included in refinement with constant isotropic temperature factors of 0.05 \AA^2 . Anisotropic refinement resulted in unacceptable geometries of the *o*-nitro group of dnp2 and appreciable densities in its neighbourhood. Omission of this group in the refinement revealed a pattern of electron densities in the difference synthesis, which could be interpreted as a disorder of the *o*-nitro group over two sites. The pertaining atoms were included in the refinement with isotropic thermal parameters. Because of the large number of parameters (728), the refinement (on F) was carried out in five blocks containing the molecular entities dnp1 + Ba, dnp2, phen1, phen2 and phen3, respectively, resulting in a final $wR \{ = \sum w^{1/2} \Delta F / \sum w^{1/2} F_o \} = 0.034$ with $w = 1.444 / [\sigma^2(F_o) + 0.000435 F_o^2]$. The occupancy ratio of the disordered nitro group refined to 0.818 and the isotropic extinction parameter converged to 2.0×10^{-8} . Except for regions of positive and negative electron densities of 0.75 e \AA^{-3} at about 1.0 \AA from Ba, the final difference map was featureless. Average shift to error ratio for non-H parameters 0.3, for H atoms 0.5. Scattering factors from *International Tables for X-ray Crystallography* (1974) and anomalous-dispersion terms from Cromer & Liberman (1970). All calculations carried out with an in-house Eclipse S/230 mini-computer with *ILIAS* (structure determination and refinement) (Spek, 1982a) and the Cyber-175 computer of the University of Utrecht with the programs from the *EUCLID* package (molecular geometry and illustrations) (Spek, 1982b).*

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, H-atom coordinates and ligand bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38734 (48 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1, a view of the molecular complex is shown in Fig. 1.

Ba is ninefold coordinated to six N atoms of the three bidentate phen ligands and to three O atoms, the phenolic and an *o*-nitro-group O atom of the bidentate dnp1 ligand, and to the phenolic O of the monodentate dnp2 ligand. The coordination of Ba can be classified as a mono-capped distorted square antiprism, as can be seen in Fig. 2. In the complex the two dnp ligands occupy *trans* positions with an interplanar angle of $62.6 (1)^\circ$, and the same holds for the phen1 and phen2 ligands which are almost perpendicular [angle of $86.0 (1)^\circ$], and the phen3 ligand is accommodated in the ligating position between dnp2 and phen2 with interplanar angles of $84.5 (1)$ and $83.3 (1)^\circ$, respectively. The geometries within the Ba coordination sphere as well as those of the five ligands are listed in Table 2.

The distances between Ba and phenolic O(1) of dnp1 [$2.697 (3) \text{ \AA}$] and phenolic O(6) of dnp2 [$2.602 (4) \text{ \AA}$] are shorter than those involving O(2) of the *o*-nitro group of dnp1 and the six N atoms of the phen ligands which lie within the range $2.906 (3)$ – $2.967 (3) \text{ \AA}$. The

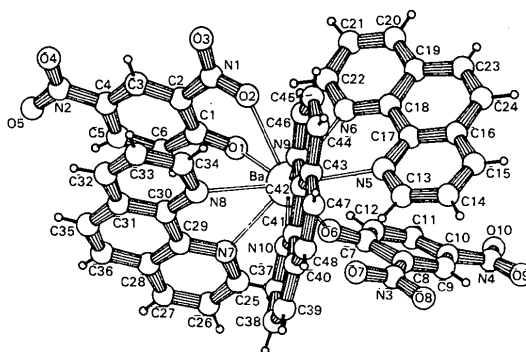


Fig. 1. A perspective view of the complex bis(2,4-dinitrophenolato)tris(1,10-phenanthroline)barium(II) with atom numbering; H atoms are numbered according to atoms to which they are attached.

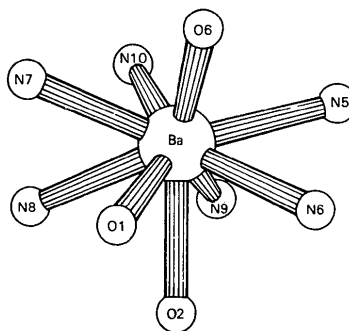


Fig. 2. View of the Ba coordination.

Table 1. Atomic coordinates and thermal parameters ($\text{\AA}^2 \times 10^3$)

Least-squares-derived standard deviations of the least significant figures are given in parentheses in all tables.

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{eq}^* |
|--------|-------------|-------------|-------------|------------|
| Ba | 0.79785 (2) | 0.39777 (1) | 0.24789 (1) | 3.38 (1) |
| O(1) | 0.6797 (3) | 0.3214 (2) | 0.3382 (2) | 5.0 (1) |
| O(2) | 0.5944 (3) | 0.4411 (2) | 0.3280 (2) | 6.0 (1) |
| O(3) | 0.4707 (4) | 0.4645 (2) | 0.4105 (3) | 8.9 (1) |
| O(4) | 0.5403 (5) | 0.3918 (2) | 0.6598 (3) | 8.9 (1) |
| O(5) | 0.6379 (5) | 0.3053 (3) | 0.6803 (2) | 9.6 (1) |
| N(1) | 0.5509 (4) | 0.4318 (2) | 0.3890 (2) | 5.1 (1) |
| N(2) | 0.5952 (4) | 0.3470 (3) | 0.6385 (2) | 6.4 (1) |
| C(1) | 0.6574 (4) | 0.3287 (2) | 0.4060 (2) | 4.1 (1) |
| C(2) | 0.5972 (4) | 0.3812 (2) | 0.4361 (3) | 4.2 (1) |
| C(3) | 0.5754 (4) | 0.3861 (2) | 0.5117 (3) | 4.7 (1) |
| C(4) | 0.6157 (4) | 0.3402 (2) | 0.5591 (2) | 4.8 (1) |
| C(5) | 0.6753 (4) | 0.2884 (2) | 0.5342 (3) | 5.2 (1) |
| C(6) | 0.6946 (4) | 0.2820 (2) | 0.4605 (3) | 4.8 (1) |
| O(6) | 0.8597 (4) | 0.2995 (2) | 0.1727 (2) | 11.5 (1) |
| O(7)† | 0.9997 (6) | 0.3686 (4) | 0.1247 (4) | 8.2 (1) |
| O(7a)† | 1.0483 (8) | 0.3778 (5) | 0.0960 (5) | 8.2 (1) |
| O(8)† | 1.0434 (7) | 0.3631 (4) | 0.0085 (5) | 8.6 (1) |
| O(8a)† | 1.0265 (9) | 0.3770 (5) | -0.0223 (5) | 8.6 (1) |
| O(9) | 0.8639 (3) | 0.2066 (2) | -0.1555 (2) | 6.8 (1) |
| O(10) | 0.7636 (3) | 0.1340 (2) | -0.1072 (2) | 7.1 (1) |
| N(3)† | 0.9870 (7) | 0.3443 (4) | 0.0616 (5) | 5.9 (1) |
| N(3a)† | 1.0043 (9) | 0.3562 (5) | 0.0349 (6) | 5.9 (1) |
| N(4) | 0.8224 (3) | 0.1823 (2) | -0.1017 (2) | 4.4 (1) |
| C(7) | 0.8594 (5) | 0.2718 (3) | 0.1106 (2) | 7.1 (1) |
| C(8) | 0.9173 (4) | 0.2953 (2) | 0.0461 (3) | 5.6 (1) |
| C(9) | 0.9030 (4) | 0.2665 (2) | -0.0232 (2) | 4.3 (1) |
| C(10) | 0.8403 (3) | 0.2116 (2) | -0.0295 (2) | 3.7 (1) |
| C(11) | 0.7904 (4) | 0.1836 (2) | 0.0319 (2) | 5.3 (1) |
| C(12) | 0.8011 (4) | 0.2127 (3) | 0.0983 (2) | 6.7 (1) |
| N(5) | 0.7435 (3) | 0.4411 (2) | 0.0923 (2) | 4.7 (1) |
| N(6) | 0.5667 (3) | 0.3793 (2) | 0.1621 (2) | 4.4 (1) |
| C(13) | 0.8263 (4) | 0.4726 (2) | 0.0585 (3) | 5.9 (1) |
| C(14) | 0.8155 (5) | 0.4894 (2) | -0.0166 (3) | 6.6 (1) |
| C(15) | 0.7139 (5) | 0.4745 (2) | -0.0569 (2) | 6.4 (1) |
| C(16) | 0.6214 (4) | 0.4434 (2) | 0.0237 (2) | 5.1 (1) |
| C(17) | 0.6404 (4) | 0.4270 (2) | 0.0522 (2) | 4.2 (1) |
| C(18) | 0.5465 (3) | 0.3962 (2) | 0.0895 (2) | 4.0 (1) |
| C(19) | 0.4362 (4) | 0.3850 (2) | 0.0502 (2) | 4.8 (1) |
| C(20) | 0.3460 (4) | 0.3582 (2) | 0.0891 (3) | 6.0 (1) |
| C(21) | 0.3647 (4) | 0.3416 (2) | 0.1617 (3) | 6.2 (1) |
| C(22) | 0.4779 (4) | 0.3523 (2) | 0.1958 (2) | 5.4 (1) |
| C(23) | 0.4230 (5) | 0.4032 (2) | -0.0277 (3) | 6.2 (1) |
| C(24) | 0.5107 (5) | 0.4300 (2) | -0.0625 (2) | 5.8 (1) |
| N(7) | 0.9701 (3) | 0.3300 (1) | 0.3448 (2) | 3.9 (1) |
| N(8) | 0.8714 (3) | 0.4372 (1) | 0.4009 (2) | 4.1 (1) |
| C(25) | 1.0218 (4) | 0.2791 (2) | 0.3194 (2) | 4.7 (1) |
| C(26) | 1.0713 (4) | 0.2317 (2) | 0.3648 (2) | 5.0 (1) |
| C(27) | 1.0656 (4) | 0.2368 (2) | 0.4402 (2) | 4.8 (1) |
| C(28) | 1.0120 (3) | 0.2899 (2) | 0.4701 (2) | 4.2 (1) |
| C(29) | 0.9664 (3) | 0.3364 (2) | 0.4203 (2) | 3.6 (1) |
| C(30) | 0.9156 (3) | 0.3930 (2) | 0.4496 (2) | 3.7 (1) |
| C(31) | 0.9133 (3) | 0.4007 (2) | 0.5275 (2) | 4.5 (1) |
| C(32) | 0.8658 (4) | 0.4563 (2) | 0.5538 (2) | 5.6 (1) |
| C(33) | 0.8235 (4) | 0.5003 (2) | 0.5056 (3) | 5.9 (1) |
| C(34) | 0.8284 (4) | 0.4891 (2) | 0.4289 (2) | 5.1 (1) |
| C(35) | 0.9576 (4) | 0.3517 (2) | 0.5757 (2) | 5.4 (1) |
| C(36) | 1.0028 (4) | 0.2992 (2) | 0.5484 (2) | 5.3 (1) |
| N(9) | 0.7909 (3) | 0.5362 (1) | 0.2388 (2) | 4.1 (1) |
| N(10) | 1.0103 (3) | 0.4790 (1) | 0.2465 (2) | 4.3 (1) |
| C(37) | 1.1170 (4) | 0.4533 (2) | 0.2570 (2) | 5.1 (1) |
| C(38) | 1.2232 (4) | 0.4879 (2) | 0.2577 (2) | 5.7 (1) |
| C(39) | 1.2174 (4) | 0.5506 (2) | 0.2441 (2) | 5.4 (1) |
| C(40) | 1.1067 (4) | 0.5801 (2) | 0.2317 (2) | 4.5 (1) |
| C(41) | 1.0045 (3) | 0.5421 (2) | 0.2354 (2) | 3.9 (1) |
| C(42) | 0.8880 (3) | 0.5720 (2) | 0.2290 (2) | 3.8 (1) |
| C(43) | 0.8801 (4) | 0.6371 (2) | 0.2164 (2) | 4.6 (1) |
| C(44) | 0.7665 (4) | 0.6653 (2) | 0.2116 (2) | 5.2 (1) |
| C(45) | 0.6709 (4) | 0.6287 (2) | 0.2226 (2) | 5.5 (1) |
| C(46) | 0.6859 (4) | 0.5644 (2) | 0.2362 (2) | 4.8 (1) |
| C(47) | 0.9854 (4) | 0.6734 (2) | 0.2097 (2) | 5.6 (1) |
| C(48) | 1.0928 (4) | 0.6463 (2) | 0.2184 (2) | 5.8 (1) |

$$* U_{eq} = (U_{11} + U_{22}\sin^2\beta + U_{33} + 2U_{13}\cos\beta)/3\sin^2\beta.$$

† Atoms of the disordered nitro group are labelled N(3), O(7), O(8) with occupancy 0.55 and N(3a), O(7a), O(8a) with occupancy 0.45.

distance of Ba to O(7) [3.318 (7) Å] of the disordered *o*-nitro group of dnp2 is the only Ba–O/N distance within the range 2.97–3.78 Å, and it is therefore tempting to classify this atom as a coordinating one too. In the acetone solvate of the phen complex of barium picrate [Ba(tnp)₂(phen)₂, Postma, Kanters, Dusenber, Venkatasubramanian & Poonia, 1983], the Ba–phenolic O distances are also short, 2.702 (3) and 2.728 (3) Å. The range of the six Ba–N distances,

Table 2. Interatomic distances (Å) and selected angles (°) and torsion angles (°)

| | | | | | |
|---------------------|------------|------------------------|------------|-------------|------------|
| Ba–O(1) | 2.697 (3) | O(1)–C(1) | 1.265 (5) | O(6)–C(7) | 1.260 (6) |
| Ba–O(2) | 2.921 (4) | O(2)–N(1) | 1.240 (5) | O(7a)–N(3a) | 1.262 (14) |
| Ba–O(6) | 2.602 (4) | O(3)–N(1) | 1.219 (6) | O(7)–N(3) | 1.246 (11) |
| Ba–O(7) | 3.318 (7) | O(4)–N(2) | 1.209 (7) | O(8a)–N(3a) | 1.159 (14) |
| Ba–N(5) | 2.967 (3) | O(5)–N(2) | 1.239 (7) | O(8)–N(3) | 1.241 (12) |
| Ba–N(6) | 2.967 (3) | N(1)–C(2) | 1.445 (6) | O(9)–N(4) | 1.212 (4) |
| Ba–N(7) | 2.906 (3) | N(2)–C(4) | 1.462 (6) | O(10)–N(4) | 1.221 (5) |
| Ba–N(8) | 2.940 (3) | C(1)–C(2) | 1.426 (6) | N(3)–C(8) | 1.321 (9) |
| Ba–N(9) | 2.944 (3) | C(1)–C(6) | 1.438 (6) | N(3a)–C(8) | 1.641 (12) |
| Ba–N(10) | 2.947 (3) | C(2)–C(3) | 1.395 (7) | N(4)–C(10) | 1.441 (5) |
| | | C(3)–C(4) | 1.354 (7) | C(7)–C(8) | 1.448 (7) |
| | | C(4)–C(5) | 1.376 (7) | C(7)–C(12) | 1.427 (8) |
| | | C(5)–C(6) | 1.359 (7) | C(8)–C(9) | 1.385 (6) |
| | | | | C(9)–C(10) | 1.365 (6) |
| | | | | C(10)–C(11) | 1.398 (6) |
| | | | | C(11)–C(12) | 1.339 (6) |
| N(5)–C(13) | 1.323 (6) | N(7)–C(25) | 1.320 (5) | N(9)–C(42) | 1.350 (5) |
| N(5)–C(17) | 1.360 (5) | N(7)–C(29) | 1.364 (4) | N(9)–C(46) | 1.323 (5) |
| N(6)–C(18) | 1.356 (5) | N(8)–C(30) | 1.355 (5) | N(10)–C(37) | 1.321 (5) |
| N(6)–C(22) | 1.327 (5) | N(8)–C(34) | 1.315 (5) | N(10)–C(41) | 1.356 (5) |
| C(13)–C(14) | 1.391 (7) | C(25)–C(26) | 1.390 (6) | C(37)–C(38) | 1.402 (6) |
| C(14)–C(15) | 1.353 (7) | C(26)–C(27) | 1.362 (6) | C(38)–C(39) | 1.353 (7) |
| C(15)–C(16) | 1.395 (7) | C(27)–C(28) | 1.398 (6) | C(39)–C(40) | 1.399 (6) |
| C(16)–C(17) | 1.409 (5) | C(28)–C(29) | 1.408 (5) | C(40)–C(41) | 1.408 (5) |
| C(16)–C(24) | 1.419 (7) | C(28)–C(36) | 1.428 (5) | C(40)–C(48) | 1.433 (6) |
| C(17)–C(18) | 1.440 (5) | C(29)–C(30) | 1.443 (5) | C(41)–C(42) | 1.454 (5) |
| C(18)–C(19) | 1.409 (6) | C(30)–C(31) | 1.409 (5) | C(42)–C(43) | 1.401 (5) |
| C(19)–C(20) | 1.386 (6) | C(31)–C(32) | 1.389 (6) | C(43)–C(44) | 1.409 (6) |
| C(19)–C(23) | 1.449 (6) | C(31)–C(35) | 1.424 (6) | C(43)–C(47) | 1.424 (6) |
| C(20)–C(21) | 1.353 (7) | C(32)–C(33) | 1.341 (6) | C(44)–C(45) | 1.350 (6) |
| C(21)–C(22) | 1.398 (6) | C(33)–C(34) | 1.401 (6) | C(45)–C(46) | 1.395 (6) |
| C(23)–C(24) | 1.326 (7) | C(35)–C(36) | 1.331 (6) | C(47)–C(48) | 1.338 (7) |
| O(1)–Ba–O(2) | 57.7 (1) | O(6)–Ba–N(10) | 102.9 (1) | | |
| O(1)–Ba–O(6) | 89.2 (1) | O(7)–Ba–N(5) | 62.8 (1) | | |
| O(1)–Ba–O(7) | 132.0 (1) | O(7)–Ba–N(6) | 104.1 (1) | | |
| O(1)–Ba–N(5) | 132.0 (1) | O(7)–Ba–N(7) | 81.3 (1) | | |
| O(1)–Ba–N(6) | 77.5 (1) | O(7)–Ba–N(8) | 120.6 (1) | | |
| O(1)–Ba–N(7) | 71.2 (1) | O(7)–Ba–N(9) | 99.6 (1) | | |
| O(1)–Ba–N(8) | 74.4 (1) | O(7)–Ba–N(10) | 61.1 (1) | | |
| O(1)–Ba–N(9) | 128.4 (1) | N(5)–Ba–N(6) | 55.1 (1) | | |
| O(1)–Ba–N(10) | 141.8 (1) | N(5)–Ba–N(7) | 144.0 (1) | | |
| O(2)–Ba–O(6) | 138.5 (1) | N(5)–Ba–N(8) | 145.1 (1) | | |
| O(2)–Ba–O(7) | 166.6 (1) | N(5)–Ba–N(9) | 68.6 (1) | | |
| O(2)–Ba–N(5) | 104.0 (1) | N(5)–Ba–N(10) | 86.1 (1) | | |
| O(2)–Ba–N(6) | 67.0 (1) | N(6)–Ba–N(7) | 141.0 (1) | | |
| O(2)–Ba–N(7) | 112.0 (1) | N(6)–Ba–N(8) | 135.3 (1) | | |
| O(2)–Ba–N(8) | 68.7 (1) | N(6)–Ba–N(9) | 94.8 (1) | | |
| O(2)–Ba–N(9) | 72.2 (1) | N(6)–Ba–N(10) | 139.3 (1) | | |
| O(2)–Ba–N(10) | 118.6 (1) | N(7)–Ba–N(8) | 56.1 (1) | | |
| O(6)–Ba–O(7) | 44.8 (2) | N(7)–Ba–N(9) | 122.8 (1) | | |
| O(6)–Ba–N(5) | 78.9 (1) | N(7)–Ba–N(10) | 77.5 (1) | | |
| O(6)–Ba–N(6) | 83.0 (1) | N(8)–Ba–N(9) | 76.9 (1) | | |
| O(6)–Ba–N(7) | 73.9 (1) | N(8)–Ba–N(10) | 70.0 (1) | | |
| O(6)–Ba–N(8) | 130.0 (1) | N(9)–Ba–N(10) | 55.6 (1) | | |
| O(6)–Ba–N(9) | 141.2 (1) | | | | |
| O(2)–N(1)–C(2)–C(1) | –23.2 (6) | O(8)–N(3)–C(8)–C(7) | 175.9 (7) | | |
| O(2)–N(1)–C(2)–C(3) | 159.1 (4) | O(8)–N(3)–C(8)–C(9) | –1.5 (10) | | |
| O(3)–N(1)–C(2)–C(1) | 157.2 (4) | O(7a)–N(3a)–C(8)–C(7) | 17.5 (12) | | |
| O(3)–N(1)–C(2)–C(3) | –20.5 (6) | O(7a)–N(3a)–C(8)–C(9) | –163.8 (8) | | |
| O(4)–N(2)–C(4)–C(3) | 2.2 (7) | O(8a)–N(3a)–C(8)–C(7) | –164.3 (9) | | |
| O(4)–N(2)–C(4)–C(5) | –178.3 (5) | O(8a)–N(3a)–C(8)–C(9) | 14.4 (12) | | |
| O(5)–N(2)–C(4)–C(3) | –177.1 (5) | O(9)–N(4)–C(10)–C(9) | 0.5 (5) | | |
| O(5)–N(2)–C(4)–C(5) | 2.5 (7) | O(9)–N(4)–C(10)–C(11) | 179.0 (4) | | |
| O(7)–N(3)–C(8)–C(7) | –1.4 (10) | O(10)–N(4)–C(10)–C(9) | –178.1 (4) | | |
| O(7)–N(3)–C(8)–C(9) | –178.8 (7) | O(10)–N(4)–C(10)–C(11) | 0.4 (5) | | |

which average 2.95 (2) Å, compares well with the range of 2.881 (3)–2.934 (3) Å observed in the acetone solvate of Ba(tnp)₂(phen)₂, though the average [2.91 (2) Å] is somewhat smaller. The three N–Ba–N bidentate angles are very similar, 55.1 (1), 56.1 (1) and 55.5 (1)°, respectively, and they correspond well with the bite angles of 56.7 (1) and 56.5 (1)° in Ba(tnp)₂(phen)₂ and 55.1 (5)° in [Ba(ClO₄)₂(phen)₂(H₂O)₄](phen)₂ (Smith, O'Reilly, Kennard & White, 1977). The same holds for the O–Ba–O ligand angle involving phenolic and *o*-nitro-group O atoms, 57.7 (1) and 56.4 (1)° for the dnp and tnp complexes, respectively.

The *o*-nitro group of dnp2 is disordered over two sites with occupancies of 0.55 and 0.45, which results in unreliable geometries of both groups. The other distances and angles of dnp1 and dnp2 show a good mutual correspondence. As in other nitrophenolates the C–O distances of dnp1 [1.265 (5) Å] and dnp2 [1.260 (6) Å] are shortened compared to neutral nitrophenols by about 0.1 Å (Hough, 1976), due to delocalization of anionic charge in the aromatic ring. The C–O shortening is accompanied by a decrease of the C–C–C angle at the phenolic site of 114.0 (4)° for dnp1 and 113.8 (4)° for dnp2, relative to the average value of 120.6 (2)° observed in a series of neutral nitrophenols (Hough, 1976). The averages of C–O distances and C–C–C angles at the phenolic site of ten picrates in Table 7 of Hough (1976) amount to 1.244 (1) Å and 111.5 (1)°, respectively, which illustrates the increase of delocalization by the presence of a second *o*-nitro group.

The *o*-nitro group of dnp1 is rotated 22.1 (3)° with respect to the plane of the aromatic ring, the rotation angle of the *p*-nitro group is 3.0 (3)°. In disordered dnp2 the interplanar angles of the pertaining *o*-nitro groups are 8.7 (4) and 16.9 (4)°, respectively, that of the *p*-nitro group is 3.7 (3)°. The twisting of the nitro groups is also borne out by the pairs of torsion angles of N–O and C–C bonds relative to the N–C bonds. The benzene rings of the dnp's are moderately planar, σ_{plane} , defined as $\{\sum d_i^2/(N-3)\}^{1/2}$, being 0.011 and 0.036 Å, respectively.

The dimensions of the three phen ligands show a good mutual correspondence and also conform with values observed in the free molecule (Nishigaki, Yoshioka & Nakatsu, 1978) and in molecular complexes (Poonia, 1975; Hughes & Truter, 1972; Smith, O'Reilly, Kennard & White, 1977; Thevenet, Rodier &

Khodadad, 1978; Thevenet, Toffoli & Rodier, 1978; Wernberg & Hazell, 1980). All three phen ligands display marked deviations from planarity, σ_{plane} for phen1 and phen2 being 0.053 and 0.038 Å, respectively, whereas in phen3 two atoms, C(38) and C(39), are 0.181 (17) and 0.161 (18) Å from the best plane of the remaining 12 atoms. This puckering seems a common feature of 1,10-phenanthroline as it has also been observed in other coordinated molecules (Jones, Milburn, Sawyer & Hughes, 1981) as well as in the free molecule (Nishigaki, Yoshioka & Nakatsu, 1978).

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