Acta Cryst. (1984). C**40**, 1699–1701

Structure of Bis(*o*-nitrophenolato)barium(II), [Ba($C_6H_4NO_3$)$_2$]

By J. A. Kanters, W. J. J. Smeets and A. J. M. Duisenberg

Laboratorium voor Kristal- en Structuurchemie, 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*

(*Received* 26 *April* 1984; *accepted* 30 *May* 1984)

Abstract. $M_r = 413{\cdot}55$, monoclinic, $C2/c$, $a = 27{\cdot}23\,(2)$, $b = 6{\cdot}094\,(1)$, $c = 7{\cdot}736\,(3)$ Å, $\beta = 97{\cdot}20\,(3)^\circ$, $V = 1274\,(1)$ Å^3, $Z = 4$, $D_x = 2{\cdot}16$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 29{\cdot}41$ cm^{-1}, $F(000) = 784$, $T = 294$ K, $R = 0{\cdot}0356$ for 1407 observed reflections. Ba lies on a twofold axis and is coordinated to ten O atoms forming a distorted one-side-bicapped square antiprism; four of the coordinating atoms are phenolic. Eight out of the ten O atoms are coordinated to two Ba^{2+} ions thus constituting an intricate two-dimensional network of Ba—O interactions.

Introduction. In the course of the study of the coordination of Ba with 2,4-dinitrophenolates (dnp) and 2,4,6-trinitrophenolates (tnp) and the neutral ligand 1,10-phenanthroline (phen) we reported the structures of Ba(phen)$_3$(dnp)$_2$ (Kanters, Postma, Duisenberg, Venkatasubramanian & Poonia, 1983) and of the acetone solvate of Ba(phen)$_2$(tnp)$_2$ (Postma, Kanters, Duisenberg, Venkatasubramanian & Poonia, 1983). In both compounds all phenolic O atoms are coordinated to Ba and of the nitro groups only half of the *o*-nitro-group O atoms neighbouring the phenolic site are bonded to the metal. In order to study the coordinating properties of the *o*-nitrophenol moiety, the structure analysis of Ba *o*-nitrophenolate was undertaken.

Experimental. Crystals prepared by mixing *o*-nitrophenol and $BaCO_3$ in a 2:1 ratio in ethanol; slow evaporation at room temperature yielded reddish plate-like crystals. Crystal $0{\cdot}6 \times 0{\cdot}4 \times 0{\cdot}2$ mm. Nonius CAD-4 diffractometer, Zr-filtered Mo $K\alpha$ radiation. Because of marked anisotropic mosaic spread, reflections were measured in the $\psi \neq 0$ mode, with $\omega = (4{\cdot}00 + 0{\cdot}35\tan\theta)^\circ$, to make the diffraction profile as narrow as possible. Values of optimal ψ were calculated from azimuthal scans of three reflections as described by Duisenberg (1983). Lattice parameters from 25 reflections. 3128 intensities in two quadrants (h −36 to 36, k 0 to 8, l 0 to 10 and h −36 to 36, k 0 to −8 and l 0 to −10); 1625 independent data ($R_{\text{int}} = 0{\cdot}062$) of which 1407 above $3\sigma(I)$. ω scan, $2\theta_{\max} = 56^\circ$. Three standard reflections (513, 022, 400) measured every 40 reflections showed a variation less than 2%. Correction for absorption (max. 4·274, min. 1·592). Structure solved with Patterson and difference Fourier methods. All H atoms located from difference syntheses and included in weighted refinement with free isotropic thermal parameters. Anisotropic weighted full-matrix refinement on F gave $R = 0{\cdot}0356$, $wR = 0{\cdot}0353$ with $w^{-1} = \sigma^2(F_o) + 0{\cdot}000039F_o^2$, and $S = 2{\cdot}84$. All Δ/σ ratios below 0·0005. In final difference synthesis densities of $\pm 1{\cdot}4$ e Å^{-3} at 0·70 Å from Ba, all other features below 0·65 e Å^{-3}. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations carried out with *SHELX*76 (Sheldrick, 1976) and the *EUCLID* package (molecular geometry and illustrations) (Spek, 1982) on the CDC Cyber-175 computer of the University of Utrecht.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å$^2 \times 10^2$) *with their e.s.d.'s in parentheses*

$$U_{\text{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ba	0	0·82948 (6)	$\frac{3}{4}$	3·14 (1)
O(1)	0·0590 (1)	−0·0193 (6)	0·5168 (4)	3·9 (1)
O(2)	0·0344 (2)	0·3845 (8)	0·6071 (6)	7·2 (2)
O(3)	0·0890 (2)	0·5648 (6)	0·7692 (5)	5·5 (1)
N(1)	0·0780 (2)	0·4099 (7)	0·6708 (5)	4·0 (1)
C(1)	0·1033 (2)	0·0541 (7)	0·5583 (5)	2·9 (1)
C(2)	0·1155 (2)	0·2648 (8)	0·6307 (6)	3·3 (1)
C(3)	0·1647 (2)	0·3402 (9)	0·6697 (7)	4·0 (1)
C(4)	0·2026 (2)	0·2095 (10)	0·6373 (7)	4·7 (2)
C(5)	0·1923 (2)	−0·0017 (11)	0·5708 (6)	4·7 (2)
C(6)	0·1451 (2)	−0·0769 (9)	0·5365 (6)	3·8 (1)

Discussion. The atomic coordinates and their equivalent isotropic thermal parameters are listed in Table 1.*

---

* Lists of structure factors, anisotropic thermal parameters of the non-H atoms, H-atom parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39545 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/84/101699-03$01.50

The numbering of the atoms and a view of the molecule are given in Fig. 1(*a*). Distances and angles as well as the coordination of Ba are given in Table 2. In the structure Ba is coordinated to ten O atoms which form a one-side-bicapped distorted square antiprism, as illustrated in Fig. 1(*b*). As Ba lies on the twofold axis, the cluster of coordinating O atoms has twofold symmetry. The five O atoms of the asymmetric part of the cluster belong to three phenolate fragments which are related by a translation along **b** and an inversion coupled with a translation along **b** + **c** respectively. Two phenolates are bidentate through phenolic O and a neighbouring O of a nitro group, and through both O atoms of the nitro group respectively, and the third phenolate is monodentate through phenolic O.

As each phenolate is coordinated to three Ba^{2+} ions that are situated in the *bc* plane there is a strong two-dimensional coherence. As Fig. 2 shows, layers of Ba^{2+} ions are stacked $\frac{1}{2}a$ apart with the hydrophobic sides of the phenolates lying face to face. The Ba···O distances in the cluster range from 2·711 (3) to 3·117 (5) Å; the shortest distance outside this range is 3·715 (5) Å. The distances involving phenolic O are short, 2·711 (3) and 2·722 (3) Å, and compare well with those observed in Ba(phen)$_3$(dnp)$_2$ [2·697 (3) and 2·602 (4) Å] and in Ba(phen)$_2$(tnp)$_2$ [2·702 (3) and 2·728 (3) Å]. The two bidentate ligand angles, involving the O atoms of the nitro group [41·2 (1)°] and phenolic O and a neighbouring O of the nitro group [54·2 (1)°], are very small. The last value corresponds well to those observed in Ba(phen)$_3$(dnp)$_2$ [57·7 (1)°] and in Ba(phen)$_2$(tnp)$_2$ [56·4 (1)°].

The geometry of the *o*-nitrophenolate moiety compares satisfactorily with that reported for a number of *o*-nitrophenolate salts and complexes (Bush & Truter, 1971; Hughes, 1973, 1975; Krogh Andersen & Krogh Andersen, 1975). The phenyl ring is moderately planar [$\sigma_{\rm av}$, defined as $(\sum_i d_i^2/N{-}3)^{1/2}$, is 0·021 Å] and the planar C—NO$_2$ fragment ($\sigma_{\rm av}$ = 0·004 Å) is rotated 17·9 (3)° with respect to the phenyl ring. The distance between phenolic O(1) and O(2) of the nitro group is short [2·667 (6) Å] as has been found in other *o*-nitrophenolates (Hughes, 1973). The molecular overcrowding which would result from a planar arrangement of the substituents is relaxed by three effects: (*a*) twisting of the *ortho* nitro group, (*b*) opposite deviations of O(1) and N(1) [0·06 (1) Å] from the mean plane of the phenyl ring, (*c*) the difference in bond angles external to C(1) and C(2), O(1)—C(1)—C(2) being 125·2 (5) and N(1)—C(2)—C(3) 116·2 (5)°.

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

Ba—O(1$^{\rm iii}$)	2·711 (3)	Ba—O(2$^{\rm iii}$)	3·092 (5)
Ba—O(1$^{\rm i}$)	2·722 (3)	Ba—O(2)	3·117 (5)
Ba—O(3)	2·900 (5)		
O(1)—C(1)	1·289 (6)	C(1)—C(6)	1·418 (7)
O(2)—N(1)	1·237 (7)	C(2)—C(3)	1·413 (8)
O(3)—N(1)	1·226 (6)	C(3)—C(4)	1·352 (8)
N(1)—C(2)	1·414 (7)	C(4)—C(5)	1·401 (9)
C(1)—C(2)	1·423 (6)	C(5)—C(6)	1·359 (8)
O(1$^{\rm iii}$)—Ba—O(1$^{\rm i}$)	72·2 (1)	O(1$^{\rm i}$)—Ba—O(3$^{\rm v}$)	135·5 (1)
O(1$^{\rm iii}$)—Ba—O(3)	133·5 (1)	O(1$^{\rm i}$)—Ba—O(2$^{\rm iv}$)	126·6 (1)
O(1$^{\rm iii}$)—Ba—O(2$^{\rm iii}$)	54·2 (1)	O(1$^{\rm i}$)—Ba—O(2$^{\rm v}$)	139·3 (1)
O(1$^{\rm iii}$)—Ba—O(2)	106·1 (1)	O(3)—Ba—O(2$^{\rm iii}$)	88·2 (1)
O(1$^{\rm iii}$)—Ba—O(1$^{\rm iv}$)	129·5 (1)	O(3)—Ba—O(2)	41·2 (1)
O(1$^{\rm iii}$)—Ba—O(1$^{\rm ii}$)	91·0 (1)	O(3)—Ba—O(3$^{\rm v}$)	112·4 (1)
O(1$^{\rm iii}$)—Ba—O(3$^{\rm v}$)	77·7 (1)	O(3)—Ba—O(2$^{\rm iv}$)	64·0 (1)
O(1$^{\rm iii}$)—Ba—O(2$^{\rm iv}$)	160·8 (1)	O(3)—Ba—O(2$^{\rm v}$)	77·5 (1)
O(1$^{\rm iii}$)—Ba—O(2$^{\rm v}$)	117·7 (1)	O(2$^{\rm iii}$)—Ba—O(2)	52·2 (1)
O(1$^{\rm i}$)—Ba—O(3)	70·3 (1)	O(2$^{\rm iii}$)—Ba—O(2$^{\rm iv}$)	130·1 (1)
O(1$^{\rm i}$)—Ba—O(2$^{\rm iii}$)	71·9 (1)	O(2$^{\rm iii}$)—Ba—O(2$^{\rm v}$)	83·1 (1)
O(1$^{\rm i}$)—Ba—O(2)	80·3 (1)	O(2)—Ba—O(2$^{\rm v}$)	59·1 (1)
O(1$^{\rm i}$)—Ba—O(1$^{\rm ii}$)	140·4 (1)		
O(2)—N(1)—O(3)	119·4 (5)	N(1)—C(2)—C(3)	116·2 (5)
O(2)—N(1)—C(2)	121·2 (4)	C(1)—C(2)—C(3)	123·1 (5)
O(3)—N(1)—C(2)	119·4 (5)	C(2)—C(3)—C(4)	119·6 (5)
O(1)—C(1)—C(2)	125·2 (5)	C(3)—C(4)—C(5)	119·1 (5)
O(1)—C(1)—C(6)	121·0 (4)	C(4)—C(5)—C(6)	121·5 (5)
C(2)—C(1)—C(6)	113·8 (5)	C(1)—C(6)—C(5)	122·7 (5)
N(1)—C(2)—C(1)	120·7 (5)		

O(2)—N(1)—C(2)—C(1)	−18·0 (7)
O(2)—N(1)—C(2)—C(3)	163·1 (5)
O(3)—N(1)—C(2)—C(1)	162·7 (4)
O(3)—N(1)—C(2)—C(3)	−16·2 (7)
O(1)—C(1)—C(2)—N(1)	3·0 (7)
O(1)—C(1)—C(2)—C(3)	−178·2 (5)
C(6)—C(1)—C(2)—N(1)	−176·0 (4)
O(1)—C(1)—C(6)—C(5)	176·7 (4)
N(1)—C(2)—C(3)—C(4)	179·1 (5)

Symmetry code
(i) $x, y+1, z$
(ii) $-x, y+1, -z+\frac{3}{2}$
(iii) $-x, -y+1, -z+1$
(iv) $x, -y+1, z+\frac{1}{2}$
(v) $-x, y, -z+\frac{3}{2}$

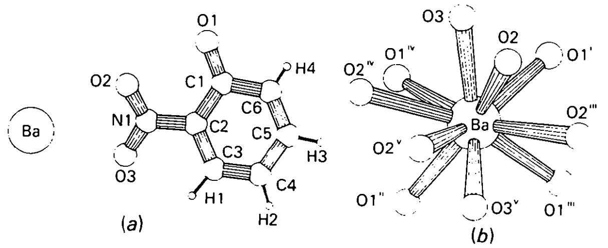
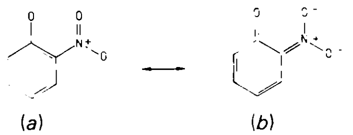


Fig. 1. (*a*) A view of the asymmetric unit with the atom numbering. (*b*) A view of the coordination of Ba, approximately perpendicular to the square bases O(3)O(2$^{\rm iii}$)O(3$^{\rm v}$)O(2$^{\rm iv}$) and O(1$^{\rm i}$)-O(1$^{\rm iii}$)O(1$^{\rm ii}$)O(1$^{\rm iv}$); O(2$^{\rm v}$), O(2) are the cap atoms. The symmetry code is given in Table 2.

The phenyl ring deviates significantly from hexagonal symmetry as is borne out by the range of distances [1·352 (8)–1·423 (6) Å] and angles [113·8 (5)–123·1 (5)°]. This distortion which is commonly found in *o*-nitrophenolates (Krogh Andersen & Krogh Andersen, 1975) has been interpreted as the effect of contributions from both the phenol and quinonoid structures (*a*) and (*b*):



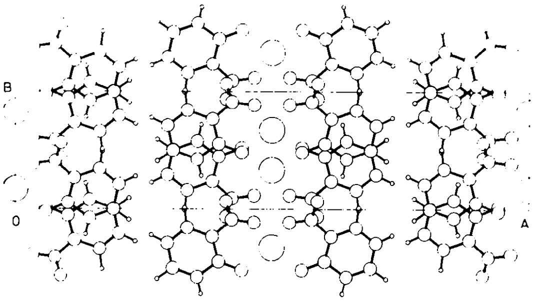


Fig. 2. Projection of the crystal structure along **c**, showing alternating polar and apolar zones.

Accordingly, there are two short bonds [C(3)–C(4) 1·352 (8) and C(5)–C(6) 1·359 (8) Å] and four longer bonds [av. 1·414 (8) Å] and the C–O [1·289 (6) Å] and C–N [1·414 (7) Å] bonds are also shorter than the corresponding bonds in aromatic phenols and nitro compounds (Bush & Truter, 1971; Hough, 1976). As in other *o*-nitrophenolates (Hough, 1976) the C–C–C angle subtended at C(1) is small [113·8 (5)°] at the expense of the angles at the *ortho* C atoms [123·1 (5) and 122·7 (5)°], whereas the other angles are close to 120°.

References

Bush, M. A. & Truter, M. R. (1971). *J. Chem. Soc. A*, pp. 745–750.

Duisenberg, A. J. M. (1983). *Acta Cryst.* A**39**, 211–216.

Hough, E. (1976). *Acta Cryst.* B**32**, 1154–1162.

Hughes, D. L. (1973). *J. Chem. Soc. Dalton Trans.* pp. 2347–2354.

Hughes, D. L. (1975). *J. Chem. Soc. Dalton Trans.* pp. 2374–2378.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Kanters, J. A., Postma, R., Duisenberg, A. J. M., Venkatasubramanian, K. & Poonia, N. S. (1983). *Acta Cryst.* C**39**, 1519–1522.

Krogh Andersen, E. & Krogh Andersen, I. G. (1975). *Acta Cryst.* B**31**, 391–393.

Postma, R., Kanters, J. A., Duisenberg, A. J. M., Venkatasubramanian, K. & Poonia, N. S. (1983). *Acta Cryst.* C**39**, 1221–1225.

Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

Spek, A. L. (1982). *Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.

Acta Cryst. (1984). C**40**, 1701–1704

Structure of Bis(2,4-dinitrophenolato)bis(triethanolamine)barium(II),* $[Ba(C_6H_3N_2O_5)_2(C_6H_{15}NO_3)_2]$

By J. A. Kanters and W. J. J. Smeets

Laboratorium voor Kristal- en Structuurchemie, 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*

(*Received* 26 *April* 1984; *accepted* 30 *May* 1984)

Abstract. $M_r = 801 \cdot 91$, monoclinic, $P2_1/c$, $a = 7 \cdot 418$ (8), $b = 17 \cdot 884$ (10), $c = 25 \cdot 007$ (13) Å, $\beta = 100 \cdot 25$ (7)°, $V = 3265$ (4) Å^3, $Z = 4$, $D_x = 1 \cdot 63$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0 \cdot 71069$ Å, $\mu = 11 \cdot 93$ cm^{-1}, $F(000) = 1616$, $T = 294$ K, $R = 0 \cdot 039$ for 5930 observed reflections. Ba is bonded to six O atoms and two N atoms of the two triethanolamines (tea's) and to one *o*-nitro-group O of one of the dinitrophenolates (dnp1). The dnp2 molecule is not coordinated at all. All tea O atoms are hydrogen-bond donors; the phenolic O atoms of dnp1 and dnp2 accept two and three hydrogen bonds respectively.

Introduction. Recently we reported the structure analyses of two Ba complexes, in which Ba is coordinated to picric acid and phenanthroline (Postma, Kanters, Duisenberg, Venkatasubramanian & Poonia, 1983) and to 2,4-dinitrophenol and phenanthroline (phen) (Kanters, Postma, Duisenberg, Venkatasubramanian & Poonia, 1983). In order to study the coordination properties of Ba with respect to other powerful ligands and particularly to compare the coordinating capacity of nitrophenols, we undertook the structure determination of the title complex.

Experimental. Crystals obtained from the Chemistry Department, University of Indore, India. Rod-shaped

---

* Triethanolamine is 2,2′,2″-nitrilotriethanol.

0108-2701/84/101701-04$01.50