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Acta Cryst. (1988). **C44**, 1405–1408

Structure of μ -1,4,7,10,13,16-Hexathiacyclooctadecane(picrato)disilver Picrate

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(Received 19 October 1987; accepted 11 April 1988)

Abstract. $[\text{Ag}_2(\text{C}_6\text{H}_2\text{N}_3\text{O}_7)(\text{C}_{12}\text{H}_{24}\text{S}_6)]^+ \cdot \text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$, $M_r = 1032.62$, monoclinic, $P2_1/c$, $a = 14.579$ (7), $b = 16.030$ (5), $c = 15.985$ (8) Å, $\beta = 110.67$ (3)°, $V = 3495$ (3) Å³, $Z = 4$, $D_m = 1.95$, $D_x = 1.962$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 15.26$ cm⁻¹, $F(000) = 2064$, $T = 293$ K, final $R = 0.036$ for 5669 observed reflections. There are two crystallographically different Ag atoms, Ag(1) and Ag(2), on opposite sides of the weighted mean plane through the non-H atoms of the asymmetric macrocyclic ligand (18S6) at distances of 1.395 (2) and -1.909 (2) Å, respectively, from it. The coordination polyhedron of Ag(1) is a distorted trigonal bipyramid with four S atoms at distances of 2.540 (1), 2.557 (1), 2.775 (2) and 3.005 (2) Å and the phenolic O atom from one picrate anion (pic) at a distance of 2.481 (3) Å from Ag(1). Ag(2) has a tetrahedrally distorted coordination with Ag(2)–S distances of 2.439 (2), 2.563 (2), 2.624 (1) and 2.671 (1) Å. All six ligand S atoms are engaged in the metal coordination but two of them are shared between adjacent Ag polyhedra causing polymeric chains of $[\text{Ag}_2(18\text{S}6)(\text{pic})]^+$ cations running along c .

Introduction. Previous studies of complex formation of silver with potentially tetradentate and hexadentate macrocyclic polythiaethers 1,4,8,11-tetrathiacyclooctadecane (14S4) and 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) have shown that silver(I) picrate with these ligands forms various complexes (Sevdić, Fekete & Meider, 1980) whose composition depends on the ratio of silver(I) picrate to ligand in the solution. Complexes corresponding to the formula $[\text{Ag}(14\text{S}4)(\text{pic})]$, $[\text{Ag}_2(14\text{S}4)(\text{pic})_2]$, $[\text{Ag}(18\text{S}6)(\text{pic})]$, $[\text{Ag}_2(18\text{S}6)(\text{pic})_2]$ and $[\text{Ag}_3(18\text{S}6)(\text{pic})_3]$ have been isolated.

As a continuation of our investigation on the coordination mode of macrocyclic polythiaethers (Herceg, Matković, Sevdić, Matković-Čalogović & Nagl, 1984; Galešić, Herceg & Sevdić, 1986) the crystal

structure of the $[\text{Ag}_2(18\text{S}6)(\text{pic})_2]$ complex has been investigated.

Experimental. The compound was prepared as described previously (Sevdić, Fekete & Meider, 1980). Crystals suitable for X-ray analysis were obtained by recrystallization from acetonitrile. D_m by flotation in a mixture of CCl_4 and CHBr_3 . Intensity data collected from a crystal of dimensions $0.25 \times 0.25 \times 0.34$ mm on a Philips PW1100 four-circle diffractometer, θ - 2θ scanning technique, scan width 1.60° , scan rate $0.04^\circ \text{ s}^{-1}$. Unit-cell parameters obtained from least-squares analysis of 20 reflections with 2θ values ranging from 10 to 15° . From absent reflections $k0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$ the space group $P2_1/c$ was determined. Out of 6931 reflections scanned within a quadrant $\pm h, k, l$ (h 19, -20; k 22; l 21) up to $(\sin \theta)/\lambda = 0.70 \text{ \AA}^{-1}$, 6704 unique reflections were classified as observed. Three standard reflections ($\bar{4}02$, 006 , 060) measured every 2 h showed an average variation of 1%. Corrections applied for Lorentz and polarization effects. No corrections for absorption or extinction. Two crystallographically different Ag atoms located by heavy-atom method, all other non-H atoms from Fourier maps. H atoms located from a difference map. In final calculations four reflections (020 , $\bar{4}04$, $\bar{7}24$, $\bar{7}44$) strongly affected by extinction were rejected. Block-diagonal least-squares refinement on F for the 5669 remaining reflections with $I > 3\sigma(I)$. Parameters of non-H atoms refined anisotropically, those of H atoms isotropically and separately in the subsequent cycles (470 and 113 parameters refined, respectively); R and wR 0.036 and 0.041, respectively; function minimized $\sum w(|F_o| - |F_c|)^2$ with $w = 1.00/\sigma^2(F_o)$ giving $S = 1.23$; $(\Delta/\sigma)_{\text{max}} = 0.14$. Final difference map revealed residuals between -0.55 and 0.49 e \AA^{-3} except for two irregular maxima of 3.91 and 1.54 e \AA^{-3} near the Ag atoms. Scattering factors of Cromer & Mann (1968) for non-H

and those of Stewart, Davidson & Simpson (1965) for H atoms; anomalous-dispersion factors from Cromer & Liberman (1970). Calculations performed mainly with XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on a Univac 1110 computer at the University Computing Centre in Zagreb.

Discussion. The final atomic parameters are listed in Table 1* and selected bond lengths and angles involving non-H atoms in Table 2. The ORTEP diagrams (Johnson, 1965) show complexation of the Ag atoms and endocyclic macrocycle torsion angles (Fig. 1) and picrate anions (Fig. 2) with the corresponding atom numbering.

It has been shown that 1,4,7,10,13,16-hexathia-cyclooctadecane could be a hexadentate ligand encapsulating metal ions with octahedral coordination: in [Ni(18S6)](pic)₂ (Hints, Hartman & Cooper, 1983), [Co(18S6)](pic)₂ (Hartman, Hints & Cooper, 1984, 1986), [Hg(18S6)](pic)₂ (Herceg, Matković-Čalogović, Matković & Sevdic, 1984), and crystals of [Cu(18S6)](pic)₂ (Hartman & Cooper, 1986; Herceg, Matković-Čalogović, Sevdic & Matković, 1987).

In [Cu(18S6)](BF₄) the macrocycle encircles the metal ion giving [Cu(18S6)]⁺ and Cu^I adopts a severely distorted tetrahedral coordination, leaving two S atoms uncoordinated (Hartman & Cooper, 1986).

Binuclear coordination has been found in the crystal structures of the complexes [Cu₂(18S6)(NCMe)₂](ClO₄)₂ and [Rh₂(η -C₅Me₅)₂Cl₂(18S6)](BPh₄)₂. In both cases, cations incorporating the macrocycle exhibit imposed C_i(1) symmetry and consist of two identically bound metal ions, each coordinated to three S atoms of the macrocycle in the case of the Cu^I complex (Gould, Lavery & Schröder, 1985) and to two S atoms in the case of the Rh^{III} complex (Bell, Blake, Schröder & Stephenson, 1986).

In the crystal structure of the compound chemically defined as [(HgCl₂)₂(18S6)].4H₂O, an infinite network of 18S6 rings connected by HgCl₂ units has been found. All S atoms are engaged in the coordination around the Hg atoms whose coordination number is five (Herceg & Golič, 1981).

In the case of Ag complexes of 18S6 the [Ag₃(18S6)(pic)₃] complex (Sevdic, Fekete & Meider, 1980) has been transformed by recrystallization into the [Ag₂(18S6)(pic)](pic) complex, in which there are two crystallographically different Ag atoms. The coordination polyhedron of Ag(1) could be described as a

Table 1. Fractional positional parameters ($\times 10^4$; $\times 10^5$ for Ag and S) and equivalent isotropic temperature factors ($\times 10^2$) for non-H atoms

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{Å}^2)$
Ag(1)	29599 (3)	73313 (2)	36658 (2)	4.29 (1)
Ag(2)	21943 (2)	78581 (2)	4866 (2)	4.78 (1)
S(1)	22348 (8)	58828 (7)	36120 (7)	4.01 (4)
S(4)	6364 (7)	71999 (7)	42389 (6)	3.83 (3)
S(7)	22750 (8)	87950 (6)	36967 (7)	3.81 (4)
S(10)	26363 (8)	93641 (7)	11503 (7)	4.09 (4)
S(13)	40068 (8)	77904 (7)	6521 (7)	4.14 (4)
S(16)	28478 (7)	69061 (6)	19494 (6)	3.54 (3)
O(1A)	4579 (2)	7888 (2)	3751 (2)	4.0 (1)
O(21A)	4857 (3)	6248 (2)	4127 (2)	6.0 (2)
O(22A)	6008 (3)	5871 (2)	5328 (3)	7.3 (2)
O(41A)	8297 (2)	7742 (2)	7226 (2)	6.2 (1)
O(42A)	8285 (3)	9042 (2)	6879 (3)	7.8 (2)
O(61A)	4622 (3)	9695 (3)	4065 (3)	10.5 (2)
O(62A)	5841 (5)	9727 (3)	3653 (4)	13.6 (4)
O(1B)	224 (2)	7297 (2)	1266 (2)	4.6 (1)
O(21B)	-100 (3)	5651 (2)	858 (3)	8.2 (2)
O(22B)	-1442 (3)	5296 (2)	-146 (3)	8.1 (2)
O(41B)	-3523 (3)	7190 (2)	-2193 (2)	7.3 (2)
O(42B)	-3381 (3)	8514 (2)	-1954 (3)	8.0 (2)
O(61B)	-661 (4)	8993 (2)	1562 (3)	8.8 (2)
O(62B)	57 (3)	9283 (3)	659 (3)	8.8 (2)
N(2A)	5564 (3)	6411 (2)	4798 (2)	4.1 (1)
N(4A)	7943 (2)	8334 (2)	6732 (2)	4.7 (1)
N(6A)	5414 (3)	9440 (2)	4089 (3)	5.6 (2)
N(2B)	-854 (3)	5834 (2)	264 (2)	4.7 (1)
N(4B)	-3106 (3)	7799 (3)	-1751 (2)	5.1 (2)
N(6B)	-512 (3)	8871 (2)	883 (2)	4.7 (1)
C(2)	919 (3)	5993 (2)	3030 (3)	3.9 (1)
C(3)	382 (3)	6202 (3)	3661 (3)	4.2 (2)
C(5)	469 (3)	7969 (3)	3369 (3)	4.4 (2)
C(6)	1053 (3)	8754 (3)	3746 (3)	4.4 (2)
C(8)	1947 (3)	9051 (3)	2513 (3)	4.5 (2)
C(9)	2863 (3)	9287 (3)	2350 (3)	4.5 (2)
C(11)	3903 (3)	9403 (3)	1201 (3)	5.0 (2)
C(12)	4490 (3)	8603 (3)	1483 (3)	4.3 (2)
C(14)	4369 (3)	6803 (3)	1239 (3)	4.2 (2)
C(15)	4115 (3)	6697 (3)	2072 (3)	3.7 (1)
C(17)	2310 (3)	5874 (3)	1862 (3)	4.5 (2)
C(18)	2576 (4)	5398 (3)	2732 (3)	4.9 (2)
C(1A)	5358 (3)	7942 (2)	4407 (2)	3.0 (1)
C(2A)	5890 (3)	7274 (2)	4984 (3)	3.1 (1)
C(3A)	6713 (3)	7407 (3)	5732 (3)	3.4 (1)
C(4A)	7078 (3)	8201 (3)	5943 (3)	3.5 (1)
C(5A)	6663 (3)	8876 (3)	5401 (3)	3.8 (1)
C(6A)	5842 (3)	8733 (2)	4674 (2)	3.4 (1)
C(1B)	-549 (3)	7362 (2)	616 (2)	3.4 (1)
C(2B)	-1111 (3)	6700 (2)	35 (3)	3.4 (1)
C(3B)	-1925 (3)	6846 (3)	-720 (3)	3.8 (1)
C(4B)	-2250 (3)	7648 (3)	-956 (3)	3.9 (1)
C(5B)	-1796 (3)	8325 (3)	-432 (3)	3.9 (1)
C(6B)	-1005 (3)	8161 (2)	319 (3)	3.5 (2)

distorted trigonal bipyramid (Fig. 1, Table 2) with its equatorial plane occupied by the phenolic O(1A) atom from one picrate anion and the S(1) and S(7) atoms from the macrocycle molecule. In the apical positions are S(16) and S(13ⁱ) from another macrocycle molecule. It is assumed that the latter atom is coordinated to Ag(1) in spite of the long Ag(1)—S(13ⁱ) distance of 3.005 (2) Å in accord with the recently reported Ag—S bond distances of 3.017 (8) and 3.106 (8) Å (Corradi Bonamartini, Fava Gasparri, Ferrari Belicchi & Nardelli, 1987). The Ag(1) atom is slightly shifted from the equatorial plane by 0.020 (2) Å to the side of the apical S(16) atom and the Ag(1)—S(16) distance is 2.775 (2) Å. The angle at Ag(1) involving the apical S(16) and S(13ⁱ) atoms being 149.25 (4)°, and the angles between the equatorial plane and the lines

* Lists of structure factors, anisotropic thermal parameters, mean planes, H-atom coordinates, all bond lengths and angles and details of some C—H...O contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44954 (69 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected bond lengths (Å) and angles (°) of non-H atoms

Ag(1)—S(1)	2.540 (1)	S(7)—C(6)	1.812 (5)
Ag(1)—S(7)	2.557 (1)	S(7)—C(8)	1.828 (5)
Ag(1)—S(16)	2.775 (2)	S(10)—C(9)	1.832 (5)
Ag(1)—S(13 ⁱ)	3.005 (2)	S(10)—C(11)	1.821 (6)
Ag(1)—O(1A)	2.481 (3)	S(13)—C(12)	1.816 (5)
Ag(2)—S(10)	2.624 (1)	S(13)—C(14)	1.820 (5)
Ag(2)—S(13)	2.563 (2)	S(16)—C(15)	1.819 (4)
Ag(2)—S(16)	2.671 (1)	S(16)—C(17)	1.815 (5)
Ag(2)—S(4 ⁱⁱ)	2.439 (2)	C(2)—C(3)	1.516 (7)
S(1)—C(2)	1.821 (4)	C(5)—C(6)	1.520 (6)
S(1)—C(18)	1.823 (6)	C(8)—C(9)	1.496 (7)
S(4)—C(3)	1.819 (4)	C(11)—C(12)	1.519 (6)
S(4)—C(5)	1.810 (5)	C(14)—C(15)	1.513 (7)
		C(17)—C(18)	1.512 (7)
O(1A)—C(1A)	1.248 (4)	O(1B)—C(1B)	1.238 (4)
N(2A)—C(2A)	1.460 (5)	N(2B)—C(2B)	1.451 (5)
N(4A)—C(4A)	1.451 (4)	N(4B)—C(4B)	1.453 (5)
N(6A)—C(6A)	1.462 (5)	N(6B)—C(6B)	1.472 (5)
C(1A)—C(2A)	1.447 (5)	C(1B)—C(2B)	1.456 (5)
C(2A)—C(3A)	1.379 (5)	C(2B)—C(3B)	1.381 (5)
C(3A)—C(4A)	1.376 (6)	C(3B)—C(4B)	1.376 (6)
C(4A)—C(5A)	1.385 (5)	C(4B)—C(5B)	1.387 (6)
C(5A)—C(6A)	1.361 (5)	C(5B)—C(6B)	1.365 (5)
C(6A)—C(1A)	1.441 (5)	C(6B)—C(1B)	1.445 (5)
S(1)—Ag(1)—S(7)	132.74 (5)	C(6)—S(7)—C(8)	98.7 (2)
S(1)—Ag(1)—O(1A)	134.99 (7)	C(9)—S(10)—C(11)	98.7 (2)
S(7)—Ag(1)—O(1A)	92.25 (7)	Ag(2)—S(13)—Ag(1 ⁱⁱ)	76.88 (3)
S(16)—Ag(1)—S(1)	82.15 (4)	C(12)—S(13)—C(14)	106.2 (2)
S(16)—Ag(1)—S(7)	110.93 (4)	Ag(1)—S(16)—Ag(2)	127.13 (5)
S(16)—Ag(1)—O(1A)	82.28 (7)	C(15)—S(16)—C(17)	103.6 (2)
S(16)—Ag(1)—S(13 ⁱ)	149.25 (4)	S(1)—C(2)—C(3)	112.3 (3)
S(13 ⁱ)—Ag(1)—S(1)	91.52 (4)	C(2)—C(3)—S(4)	118.1 (3)
S(13 ⁱ)—Ag(1)—S(7)	95.47 (4)	S(4)—C(5)—C(6)	110.8 (3)
S(13 ⁱ)—Ag(1)—O(1A)	81.18 (7)	C(5)—C(6)—S(7)	115.8 (3)
S(10)—Ag(2)—S(13)	84.27 (4)	S(7)—C(8)—C(9)	108.3 (3)
S(10)—Ag(2)—S(16)	102.18 (4)	C(8)—C(9)—S(10)	110.9 (3)
S(10)—Ag(2)—S(4 ⁱⁱ)	112.99 (4)	S(10)—C(11)—C(12)	116.1 (4)
S(13)—Ag(2)—S(16)	81.33 (4)	C(11)—C(12)—S(13)	110.8 (3)
S(13)—Ag(2)—S(4 ⁱⁱ)	135.35 (5)	S(13)—C(14)—C(15)	115.8 (3)
S(16)—Ag(2)—S(4 ⁱⁱ)	129.48 (4)	C(14)—C(15)—S(16)	116.0 (2)
C(2)—S(1)—C(18)	99.9 (2)	S(16)—C(17)—C(18)	115.2 (3)
C(3)—S(4)—C(5)	105.1 (2)	C(17)—C(18)—S(1)	116.3 (3)
C(2A)—C(1A)—C(6A)	111.5 (3)	C(2B)—C(1B)—C(6B)	110.3 (3)
C(1A)—C(2A)—C(3A)	123.0 (3)	C(1B)—C(2B)—C(3B)	123.4 (4)
C(2A)—C(3A)—C(4A)	119.9 (3)	C(2B)—C(3B)—C(4B)	120.3 (4)
C(3A)—C(4A)—C(5A)	121.6 (3)	C(3B)—C(4B)—C(5B)	121.4 (3)
C(4A)—C(5A)—C(6A)	117.4 (4)	C(4B)—C(5B)—C(6B)	117.1 (4)
C(1A)—C(6A)—C(5A)	126.3 (3)	C(1B)—C(6B)—C(5B)	127.4 (3)

Symmetry code: (i) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$.

through Ag(1)—S(16) and Ag(1)—S(13ⁱ) being 68.1 (1) and 79.9 (1)°, respectively, show a severe distortion of the trigonal bipyramid. Coordination of Ag(2) is distorted tetrahedral and involves S(10), S(13), S(16) and S(4ⁱⁱ) at an Ag(2)—S(4ⁱⁱ) distance of 2.439 (2) Å which is the shortest Ag—S distance in the complex (Fig. 1, Table 2). The distortion of the Ag(2) tetrahedron could be shown by comparing its six S—Ag—S bond angles which range from 81.33 (4) to 135.35 (5)°: two of them are considerably smaller than, two are roughly close to and two are considerably larger than the angle of the regular tetrahedron. The next closest O or S atoms to Ag are O(21A) and S(4) at distances of 3.126 (4) and 3.814 (2), respectively, from Ag(1) and O(1B) and S(1ⁱⁱ) at 3.625 (4) and 3.631 (2) Å from Ag(2), respectively.

As shown in Fig. 1, the macrocycle is bonded to four Ag atoms: Ag(1), Ag(2), Ag(1ⁱⁱ) and Ag(2ⁱ). Four macrocycle S atoms are coordinated to one of the Ag atoms, while the S(13) and S(16) atoms are shared

between the Ag(2), Ag(1ⁱⁱ) and Ag(1), Ag(2) polyhedra, respectively, causing polymeric chains of [Ag₂(18S6)(pic)]⁺ cations with alternating Ag and S atoms, running along *c*. The shortest Ag...Ag distances are Ag(2)...Ag(1ⁱⁱ) 3.479 (2) and Ag(1)...Ag(2) 4.877 (3) Å. Ag(1) and Ag(2) are on opposite sides with respect to the weighted mean plane (*M*) through the non-H atoms of the macrocycle, at distances of 1.395 (2) and -1.909 (2) Å, respectively, from it. The atoms defining the mean plane *M* deviate from it within ±1.100 (5) Å.

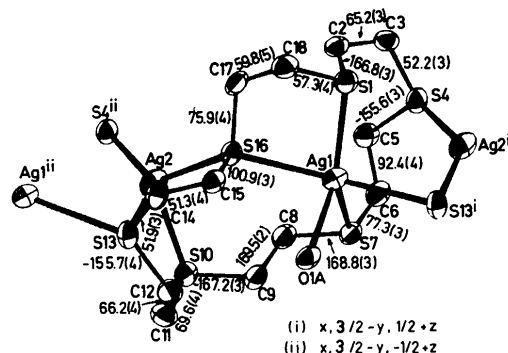
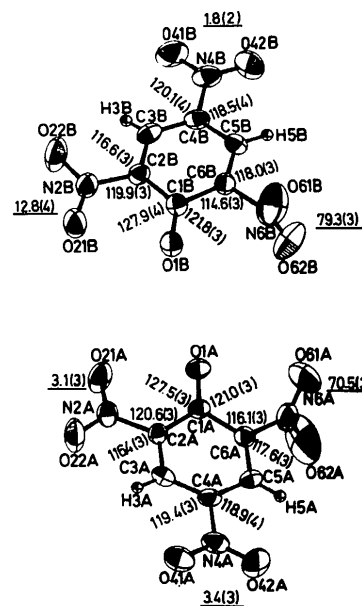


Fig. 1. Diagram showing the coordination of the Ag atoms, endocyclic torsion angles of the macrocyclic ligand (°) and the atom numbering. Ellipsoids are at the 50% probability level. For clarity the H atoms are omitted.

Fig. 2. Diagram of the A and B picrate anions viewed along *c* showing the exocyclic O—C—C and N—C—C bond angles, the interplanar angles (underlined) between the nitro groups and the corresponding benzene mean planes and the picrate atom numbering. Ellipsoids are at the 50% probability level.

The macrocycle C—C bond lengths ranging from 1.496 (7) to 1.520 (6) Å show some shortening with respect to the single C—C bond, as often observed in crown structures (Hartman, Wolf, Foxman & Cooper, 1983; Herceg, Matković, Sevdic, Matković-Čalogović & Nagl, 1984). On the other hand, the C—C—S bond angles ranging from 108.3 (3) to 118.1 (3)° [average 113.9 (3)°] show some enlargement with respect to the regular tetrahedral angle. The S—C bond lengths range from 1.810 (5) to 1.832 (5) Å, while the C—S—C bond angles range from 98.7 (2) to 106.2 (2)°. It is known that synclinal C—C—S—C and antiperiplanar S—C—C—S torsion angles are preferred in crown polythiaethers, because the synclinal S—C—C—S angles are energetically unfavourable (Hartman, Wolf, Foxman & Cooper, 1983; Wolf, Hartman, Storey, Foxman & Cooper, 1987). In this macrocycle complex even five (of six) S—C—C—S angles are not antiperiplanar (Fig. 1), indicating strain within the ring.

The geometries of the coordinated (*A*) and uncoordinated (*B*) picrate anion are similar (Table 2, Fig. 2). Their partially quinoid character is indicated by the short C—O bonds of 1.248 (4) and 1.238 (4) Å and the relatively long ring C—C bonds adjacent to them ranging from 1.441 (5) to 1.456 (5) Å. However, the other C—C bonds, ranging from 1.361 (5) to 1.387 (6) Å, do not differ from each other significantly. The exocyclic O—C—C angles are significantly different in each picrate anion in a similar way: O(1*A*)—C(1*A*)—C(2*A*) 127.5 (3), O(1*A*)—C(1*A*)—C(6*A*) 121.0 (3) and O(1*B*)—C(1*B*)—C(2*B*) 127.9 (4), O(1*B*)—C(1*B*)—C(6*B*) 121.8 (3)°. The C atoms of the picrate *A* and *B* anions deviate from their corresponding weighted *A* and *B* mean planes within ± 0.028 (4) and ± 0.027 (5) Å, respectively. The interplanar angle between these planes is 165.8 (2)°. The two picrate anions are on the opposite sides of the macrocycle molecule. The *A*/*M* and *B*/*M* interplanar angles are 87.7 (1) and 85.5 (1)°, respectively. In accord with earlier reports (Robertson & Tooptakong, 1985; Nardelli, Pelizzi, Vitali, Bordini, Plazzi & Vitali, 1987), the *p*-nitro groups are nearly coplanar with the corresponding benzene *A* and *B* mean planes with corresponding interplanar angles of 3.4 (3) and 1.8 (2)°, respectively, while the *o*-nitro groups are differently twisted with respect to the benzene planes on account of strain between them and the phenolic O atoms. The interplanar angles of the *o*-nitro groups attached at the C(2*A*) and C(6*A*) atoms and the *A* benzene mean plane are 3.1 (3) and 70.5 (3)°, while the angles of the *o*-nitro groups attached at the C(2*B*) and C(6*B*) atoms and the *B* benzene mean plane are 12.8 (4) and 79.4 (3)°, respectively. As expected, the two smallest interplanar angles correspond to the largest O—C—C bond angles mentioned above and *vice*

versa (Fig. 2), as a way of releasing the hindrance between the phenolic O atoms and the *o*-nitro groups.

Among the C—H...O contacts of the macrocycle molecule and the picrate anions C(2)...O(1*B*) 3.366 (5), C(15)...O(1*A*) 3.326 (6) and C(17)...O(21*B*) 3.166 (5) Å seem to be hydrogen bonds (deposited Table 6).

The authors thank M. Bruvo MSc for collecting diffractometer data and help during its processing, for which thanks are also due to Dr I. Vicković. This investigation was supported by the Research Council of Croatia.

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