C(19)	0.4485 (4)	0.1313 (3)	0.2097 (4)	0.077 (2)
C(20)	0.4943 (4)	0.0884 (3)	0.1570 (4)	0.084 (3)
C(21)	0.5169 (4)	0.0447 (3)	0.2175 (4)	0.095 (3)
C(22)	0.4885 (4)	0.0611 (2)	0.3090 (4)	0.061 (2)
C(23)	0.4463 (4)	0.1144 (2)	0.3069 (4)	0.061 (2)
C(24)	0.4268 (4)	0.1497 (3)	0.3953 (4)	0.082 (3)
C(25)	0.3586 (6)	0.1204 (3)	0.4686 (4)	0.108 (3)
C(26)	0.3648 (6)	0.2030 (3)	0.3656 (5)	0.120 (4)
C(27)	0.5406 (5)	0.1660 (3)	0.4393 (5)	0.108 (3)
C(28)	−0.1852 (9)	0.0224 (4)	0.3824 (6)	0.146 (4)
C(29)	−0.2335 (7)	−0.0289 (3)	0.3429 (5)	0.119 (4)
C(30)	−0.1870 (8)	−0.0341 (3)	0.2488 (5)	0.124 (4)
C(31)	−0.1527 (7)	0.0213 (3)	0.2219 (4)	0.106 (3)
C(32)	−0.2444 (6)	0.1629 (3)	0.2062 (7)	0.118 (4)
C(33)	−0.2861 (9)	0.2176 (4)	0.1789 (10)	0.172 (6)
C(34)	−0.1925 (9)	0.2538 (5)	0.1848 (9)	0.159 (6)
C(35)	−0.1098 (8)	0.2277 (3)	0.2502 (8)	0.133 (5)
C(36)	0.0357 (7)	0.1403 (7)	0.5165 (6)	0.341 (11)
C(37)	0.0220 (9)	0.1612 (4)	0.6056 (6)	0.186 (6)
C(38)	−0.0742 (9)	0.1938 (4)	0.5878 (8)	0.210 (6)
C(39)	−0.1349 (7)	0.1627 (5)	0.5116 (7)	0.170 (5)

Table 2. *Selected geometric parameters* (Å, °)

Cp indicates the centroid of the *tert*-butylcyclopentadienyl ring.

Li—O(1)	1.90 (1)	Li—O(2)	1.93 (1)
Li—O(3)	1.94 (1)	Cl—Li	2.345 (9)
Nd—Cl	2.797 (2)	Nd—C(1)	2.856 (5)
Nd—C(2)	2.744 (6)	Nd—C(3)	2.746 (5)
Nd—C(4)	2.872 (5)	Nd—C(5)	2.974 (5)
Nd—C(10)	2.894 (5)	Nd—C(11)	2.767 (7)
Nd—C(12)	2.722 (7)	Nd—C(13)	2.850 (6)
Nd—C(14)	2.962 (5)	Nd—C(19)	2.874 (6)
Nd—C(20)	2.769 (5)	Nd—C(21)	2.750 (5)
Nd—C(22)	2.865 (5)	Nd—C(23)	2.965 (5)
Nd—Cl—Li	141.4 (3)	*Cp*(1)—Nd—*Cp*(2)	118.0
Cp(2)—Nd—*Cp*(3)	115.8	*Cp*(3)—Nd—*Cp*(1)	115.7
Cl—Nd—*Cp*(1)	101.0	Cl—Nd—*Cp*(2)	98.2
Cl—Nd—*Cp*(3)	103.7		

The title complex is very sensitive to air and moisture, so all manipulations were performed using Schlenk techniques under Ar. A suitable crystal was chosen and sealed in a glass capillary. The structure was solved by Patterson methods and refined by full-matrix least squares. H atoms were located in idealized positions, 0.96 Å from the parent C atom, and were assigned fixed isotropic displacement parameters, $U = 0.05$ Å^2. All calculations were carried out on an Eclipse S/140 microcomputer with the *SHELXTL* (Sheldrick, 1983) program.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71788 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1076]

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A 1:2 Addition Compound of Cadmium Bromide with 3-Methyl-4-nitropyridine *N*-Oxide

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Abstract

catena-Poly[bis(3-methyl-4-nitropyridine *N*-oxide-*O*)cadmium-di-μ-bromo], $[Cd(C_6H_6N_2O_3)_2Br_2]$, which belongs to a group of potential nonlinear optical materials, crystallizes in the non-centrosymmetric space group *Fdd*2. The Cd atom is octahedrally coordinated to two O atoms from the *trans* 3-methyl-4-nitropyridine *N*-oxide ligands in the axial positions and four Br atoms lying in the equatorial plane. The coordination octahedra form one-dimensional chains along the short *c* axis by edge-sharing through the Br atoms, with each Cd atom located on a crystallographic diad axis.

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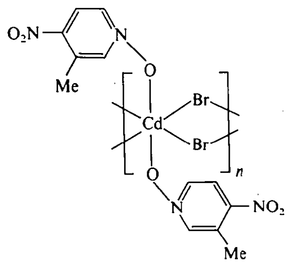
Comment

3-Methyl-4-nitropyridine *N*-oxide (pom) is one of the best electro-optical materials in the visible range (Sapriel, Hierle, Zyss & Boissier, 1989). This structure determination continues a study on the complexes of pom with metallic dihalides, which exhibit potential nonlinear optical properties (Jiang, Xu & Shao, 1985; Jiang, Xu, Tao & Yuan, 1987; Yuan, Zhang, Tao, Xu & Jiang, 1989). Previously we have reported the structures of Zn(pom)$_2$Br$_2$ (Li, Wang, Chen & Su, 1993) and Hg(pom)Br$_2$ (Hu, Shi, Li & Yang, 1992), which both crystallize in centrosymmetric space groups and exhibit zero intensity of second harmonic generation, $I_{2\omega}$. For the title compound, Cd(pom)$_2$Br$_2$ (I), however, $I_{2\omega}$ is 18 times that of potassium dihydrogen phosphate (Li, Yang, Lin, Chen, Shi & Hu, 1992).



(I)

Each Cd atom is located on a crystallographic twofold axis and is coordinated octahedrally by two O atoms attached to pyridine groups from *trans* pom ligands and four Br atoms lying in the equatorial plane (Fig. 1). The crystal structure can be described as individual chains of CdBr$_4$O$_2$ octahedra packed along the short *c* axis by edge-sharing through the Br atoms, somewhat similar to that of CdBr$_2$.4H$_2$O (Leligny & Monier, 1978). The discrete chains are stabilized by van der Waals interactions as shown in Fig. 2. The distances Cd—Br and Cd—O are comparable with those of CdBr$_2$.4H$_2$O. Differences in bond lengths between the free and complexed pom ligand are not significant (Shiro, Yamakawa & Kubota, 1977). However, the twist angle between the nitro group and the pyridine plane of the title compound is only 3.7°, which is less than that of the free ligand (16.7°) and the compounds Zn(pom)$_2$Br$_2$ (32.0, 146.2°) and Hg(pom)Br$_2$ (20.1°), and is accompanied by a short C6···O3 contact of 2.74 (2) Å.

The crystal data for Cd(pom)$_2$Br$_2$ were preliminarily reported as monoclinic, space group *Cc*, $a = 3.976\ (1)$, $b = 56.810\ (7)$, $c = 8.120\ (1)$ Å, $\beta = 104.26\ (3)°$, $Z = 4$, and the structure was refined with several non-H atoms having isotropic displacement parameters to a final $R = 0.057$ (Li, Yang, Lin, Chen, Shi & Hu, 1992). In fact the vectors [102], [010], [100] describe an orthorhombic *F*-centred cell; the revised crystal data and refined atomic parameters are reported here. Not only the lower final *R* factor, but

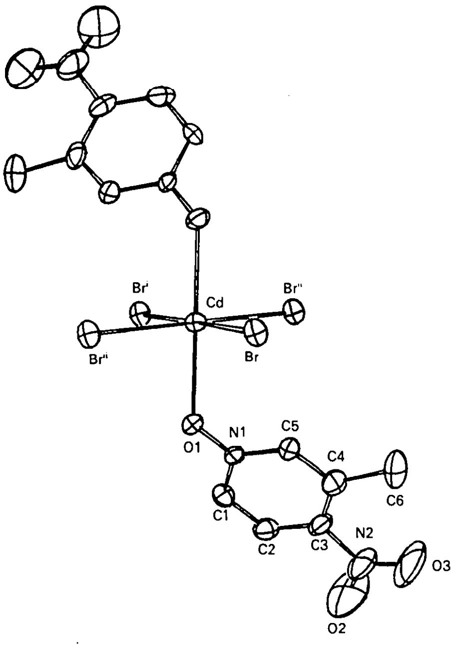


Fig. 1. Structure of the complex, showing the atom-numbering scheme. Non-H atoms are shown as displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity. The symmetry codes are defined in the footnote to Table 2.

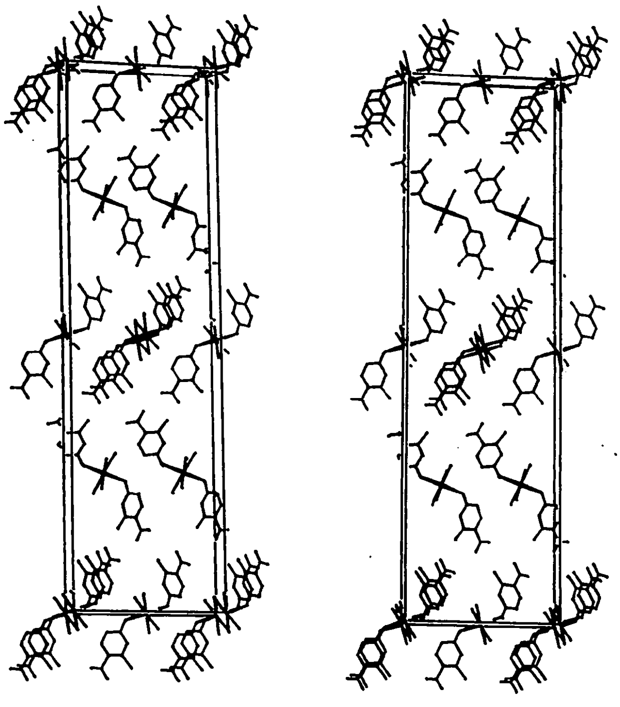


Fig. 2. Stereoview of the molecular packing viewed along the *c* axis. The *a* axis is horizontal and the *b* axis is vertical.

the lower estimated standard deviations and more regular coordination around the central Cd atom, are strong arguments in favour of the present description. This is despite the fact that the *Cc* space group also meets the essential condition of non-centrosymmetry for a nonlinear optical material.

Experimental

Crystal data

$[CdBr_2(C_6H_6N_2O_3)_2]$
$M_r = 580.47$
Orthorhombic
*Fdd*2
$a = 15.743$ (5) Å
$b = 57.011$ (25) Å
$c = 3.962$ (1) Å
$V = 3556.0$ (3.6) Å^3
$Z = 8$
$D_x = 2.168$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13$–$25°$
$\mu = 5.71$ mm^{-1}
$T = 296$ K
Needle
0.50 × 0.10 × 0.08 mm
Pale yellow

Data collection

Enraf-Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.81$, $T_{max} = 1.18$
1050 measured reflections
1050 independent reflections

887 observed reflections [$I > 3\sigma(I)$]
$\theta_{max} = 26°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 70$
$l = 0 \rightarrow 4$
2 standard reflections
frequency: 60 min
intensity variation: 1.5%

Refinement

Refinement on F
$R = 0.036$
$wR = 0.038$
$S = 1.208$
887 reflections
113 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + (0.01F_o)^2 + 1.0]$

$\Delta\rho_{max} = 0.527$ e Å^{-3}
$\Delta\rho_{min} = -0.706$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Cd	0	0	0.2305†	1.86 (1)
Br	0.04591 (6)	0.03092 (2)	0.7161 (4)	2.40 (2)
O1	0.1399 (4)	−0.01349 (9)	0.222 (3)	2.7 (1)
O2	0.3321 (7)	−0.0939 (2)	0.905 (4)	9.4 (3)
O3	0.2373 (7)	−0.1138 (1)	0.708 (5)	9.7 (4)
N1	0.1673 (5)	−0.0330 (1)	0.359 (2)	2.1 (2)
N2	0.2692 (6)	−0.0956 (1)	0.749 (4)	4.6 (2)
C1	0.2412 (6)	−0.0325 (2)	0.533 (3)	2.7 (2)
C2	0.2723 (6)	−0.0533 (2)	0.663 (3)	2.9 (2)
C3	0.2288 (6)	−0.0742 (2)	0.612 (3)	2.8 (2)
C4	0.1515 (6)	−0.0745 (2)	0.446 (3)	2.8 (2)
C5	0.1236 (6)	−0.0535 (2)	0.316 (3)	2.5 (2)
C6	0.0949 (8)	−0.0956 (2)	0.393 (4)	4.5 (3)

† Coordinate fixed to define origin

Table 2. *Selected geometric parameters* (Å, °)

Cd—Br	2.708 (1)	N1—C5	1.370 (10)
Cd—Br^{i}	2.790 (1)	N2—C3	1.476 (12)
Cd—O1	2.333 (5)	C1—C2	1.379 (13)
O1—N1	1.309 (9)	C2—C3	1.392 (13)
O2—N2	1.172 (15)	C3—C4	1.385 (14)
O3—N2	1.166 (12)	C4—C5	1.371 (13)
N1—C1	1.351 (12)	C4—C6	1.515 (13)
Br—Cd—Br^{i}	178.35 (5)	O2—N2—O3	121 (1)
Br—Cd—Br^{ii}	92.22 (2)	O2—N2—C3	119 (1)
Br—Cd—Br^{iii}	89.43 (5)	C1—N1—C5	120.8 (7)
Br^{i}—Cd—Br^{ii}	86.14 (5)	O3—N2—C3	120 (1)
O1—Cd—Br	88.4 (2)	N1—C1—C2	118.7 (8)
O1—Cd—Br^{i}	91.5 (2)	N2—C3—C2	116.4 (9)
O1—Cd—Br^{ii}	87.3 (2)	N2—C3—C4	123.0 (9)
O1—Cd—Br^{iii}	92.7 (2)	C1—C2—C3	120.5 (9)
O1—Cd—O1^{iii}	178.4 (5)	C2—C3—C4	120.6 (8)
Cd—Br—Cd^{iv}	92.22 (2)	C3—C4—C5	116.8 (8)
Cd—O1—N1	125.5 (8)	C3—C4—C6	126.2 (9)
O1—N1—C1	118.6 (7)	C5—C4—C6	117 (1)
O1—N1—C5	120.5 (7)	N1—C5—C4	122.5 (9)

Symmetry codes: (i) $-x, -y, z - 1$; (ii) $x, y, z - 1$; (iii) $-x, -y, z$; (iv) $x, y, 1 + z$.

Data collection and reduction: *SDP* (B. A. Frenz & Associates, Inc., 1982). Program(s) used to solve structure: *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP*II (Johnson, 1976). The H atoms were placed in calculated positions and were not refined. Structure refinement was based on full-matrix least-squares methods and comparison between the enantiomorphic structures was performed. All calculations were carried out on a PDP11/44 computer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71780 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1040]

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