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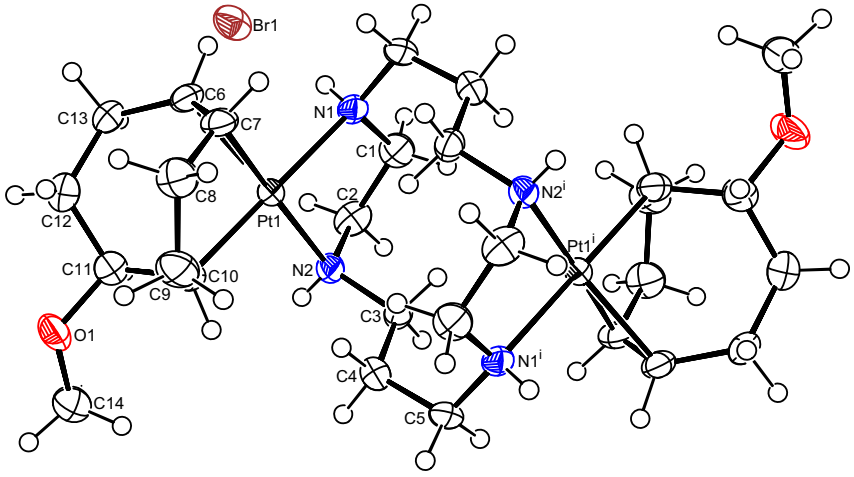
# Crystal structure of bis($\eta^2$, $\sigma^1$-8-methoxycyclooct-4-enyl)($\mu_2$-1,4,8,11-tetraazacyclotetradecane-$\kappa^4$ *N*, *N′*, *N″*, *N‴*)diplatinum(II) dibromide, $C_{28}H_{54}Br_2N_4O_2Pt_2$

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**Abstract**

$C_{28}H_{54}Br_2N_4O_2Pt_2$, monoclinic, $P2_1/n$ (no. 14), $a$ = 9.798(5) Å, $b$ = 11.389(5) Å, $c$ = 15.228(7) Å, $\beta$ = 107.148(14)°, $V$ = 1623.6(12) Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.0273, $wR_{ref}(F^2)$ = 0.0529, T = 223 K.

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The title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Colorless Block |
| Size: | 0.16 × 0.07 × 0.07 mm |
| Wavelength: | Mo*Kα* radiation (0.71073 Å) |
| $\mu$: | 11.1 mm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX CCD, $\varphi$ and $\omega$ $\varphi$ and $\omega$ scans |
| $\theta_{max}$, completeness: | 28.2°, 100 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 29323, 3987, 0.048 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\sigma(I_{obs})$, 3348 |
| $N(param)_{refined}$: | 181 |
| Programs: | Bruker,[1] SHELX,[2] ORTEP-III,[3] PLATON,[4] |

## 1 Source of materials

The pale yellow suspension of [$PtBr_2$(cod)] (cod = 1,5-cyclooctadiene; 0.1104 g, 0.238 mmol) and 1,4,8,11-tetraazacyclotetradecane (cyclam; 0.0280 g, 0.140 mmol) in methanol (10 ml) was refluxed for 3 h. After cooling, the formed precipitate was separated by filtration, washed with methanol and acetone, and dried at 60 °C, to give a white powder (0.0703 g). Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from a methanol solution at room temperature.

## 2 Experimental details

H atoms on N atoms of cyclam ligand were located from Fourier difference maps and refined isotropically; d(N–H) = 0.77(5) and 0.75(5) Å. All H atoms on C atoms were

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

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Pt1 | 0.52411 (2) | 0.32286 (2) | 0.38956 (2) | 0.02582 (5) |
| Br1 | 0.25407 (6) | 0.02174 (5) | 0.37421 (3) | 0.04306 (13) |
| O1 | 0.6683 (4) | 0.3268 (4) | 0.1480 (3) | 0.0545 (11) |
| N1 | 0.3956 (4) | 0.2718 (4) | 0.4791 (3) | 0.0280 (8) |
| H1 | 0.367 (5) | 0.211 (4) | 0.460 (3) | 0.026 (14)* |
| N2 | 0.3568 (4) | 0.4449 (3) | 0.3426 (3) | 0.0291 (9) |
| H2 | 0.347 (5) | 0.455 (5) | 0.293 (4) | 0.037 (16)* |
| C1 | 0.2600 (5) | 0.3419 (4) | 0.4535 (3) | 0.0370 (11) |
| H1A | 0.2698 | 0.4092 | 0.4950 | 0.044* |
| H1B | 0.1809 | 0.2930 | 0.4596 | 0.044* |
| C2 | 0.2285 (5) | 0.3845 (4) | 0.3554 (3) | 0.0367 (11) |
| H2A | 0.2026 | 0.3178 | 0.3131 | 0.044* |
| H2B | 0.1476 | 0.4391 | 0.3413 | 0.044* |
| C3 | 0.3771 (5) | 0.5643 (4) | 0.3859 (3) | 0.0290 (10) |
| H3A | 0.3974 | 0.5560 | 0.4526 | 0.035* |
| H3B | 0.2884 | 0.6092 | 0.3630 | 0.035* |
| C4 | 0.4978 (5) | 0.6316 (4) | 0.3657 (3) | 0.0343 (11) |
| H4A | 0.4695 | 0.6506 | 0.3001 | 0.041* |
| H4B | 0.5815 | 0.5802 | 0.3783 | 0.041* |
| C5 | 0.5412 (5) | 0.7452 (4) | 0.4203 (3) | 0.0326 (10) |
| H5A | 0.6105 | 0.7867 | 0.3965 | 0.039* |
| H5B | 0.4567 | 0.7955 | 0.4098 | 0.039* |
| C6 | 0.6175 (5) | 0.1502 (4) | 0.4006 (3) | 0.0324 (10) |
| H6 | 0.5820 | 0.0982 | 0.4411 | 0.039* |
| C7 | 0.7203 (5) | 0.2285 (4) | 0.4503 (3) | 0.0322 (10) |
| H7 | 0.7424 | 0.2187 | 0.5176 | 0.039* |
| C8 | 0.8435 (5) | 0.2809 (5) | 0.4211 (4) | 0.0429 (12) |
| H8A | 0.8894 | 0.2185 | 0.3956 | 0.051* |
| H8B | 0.9147 | 0.3126 | 0.4754 | 0.051* |
| C9 | 0.7952 (6) | 0.3785 (5) | 0.3497 (4) | 0.0458 (13) |
| H9A | 0.8501 | 0.3733 | 0.3054 | 0.055* |
| H9B | 0.8156 | 0.4548 | 0.3805 | 0.055* |
| C10 | 0.6346 (5) | 0.3709 (4) | 0.2978 (3) | 0.0369 (11) |
| H10 | 0.6019 | 0.4503 | 0.2743 | 0.044* |
| C11 | 0.5996 (6) | 0.2867 (5) | 0.2159 (4) | 0.0435 (13) |
| H11 | 0.4948 | 0.2849 | 0.1872 | 0.052* |
| C12 | 0.6535 (7) | 0.1623 (5) | 0.2379 (4) | 0.0519 (15) |
| H12A | 0.7579 | 0.1644 | 0.2624 | 0.062* |
| H12B | 0.6295 | 0.1171 | 0.1806 | 0.062* |
| C13 | 0.5942 (6) | 0.0981 (4) | 0.3064 (4) | 0.0406 (12) |
| H13A | 0.4910 | 0.0895 | 0.2783 | 0.049* |
| H13B | 0.6351 | 0.0189 | 0.3144 | 0.049* |
| C14 | 0.5942 (6) | 0.4181 (5) | 0.0908 (4) | 0.0448 (13) |
| H14A | 0.6386 | 0.4333 | 0.0428 | 0.067* |
| H14B | 0.5976 | 0.4886 | 0.1271 | 0.067* |
| H14C | 0.4955 | 0.3951 | 0.0632 | 0.067* |

positioned geometrically and allowed to ride on their parent atoms with d(C–H) = 0.99, 0.98 or 0.97 Å and $U_{iso}$ (H) = 1.2 $U_{eq}$ (C) or 1.5 $U_{eq}$ (methyl C) with the help of the SHELXL program (AFIX 13, 23 or 137 options).[2] The highest peak (2.21 e Å$^{-3}$) and the deepest hole (–1.33 e Å$^{-3}$) in the difference Fourier map are located 0.76 Å and 0.70 Å from the atom Pt1.

# 3 Comment

This contribution is part of my continuing interest in the structural chemistry of metal complexes containing cyclam ligand.[5–8] The title compound was unexpectedly obtained from the reaction of [$PtBr_2$(cod)] and cyclam in the methanol solvent under heating: during the reaction, a methoxy group was bound to one of the double-bonds of the cod ligand of the complex [$PtBr_2$(cod)], and thus the double-bond changed to a single-bond.

The title compound consists of a cationic dinuclear Pt(II) complex and two $Br^-$ counter-anions. In the cationic complex, each Pt(II) ion has a distorted square-planar coordination geometry defined by two N atoms of a tetradentate cyclam ligand and one C atom and the mid-point of the π-coordinated double-bonds of the 8-methoxycyclooct-4-enyl anionic ligand, inversion center is located at the centroid of the complex; the asymmetric unit contains one half of the compound. The anionic ligand coordinates to the Pt atom in the distorted boat conformation with the coordinated double-bond length of 1.390(7) Å, and the single-bond lengths lie in the range of 1.506(7)–1.542(7) Å. The tight N–Pt–N and C–Pt–C chelating angles of ⟨N1–Pt1–N2 = 81.57(16)° and ⟨C7–Pt1–C10 = 81.06(19)° significantly contribute the distortion of the square-plane. The Pt–N bond lengths are slightly different with d(Pt1–N1/2) = 2.190(4) and 2.107(4) Å, because of the slightly different trans effects. In the crystal structure, the complex and anions display weak inter- and intramolecular N–H···Br and C–H···O hydrogen bonds with distances of 3.013(1)–3.434(2) Å between the donor and acceptor atoms, to stabilize the three-dimensional packing.[4] It should be mentioned that the topology of a dinuclear sandwich complex with the title tetraaza ligand is rare.[9]

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