# Crystal structure of hexaaquacobalt(II) dibromide bis(hexamethylenetetramine) tetrahydrate, $[(H_2O)_6Co]Br_2 \cdot 2(C_6H_{12}N_4) \cdot 4H_2O$

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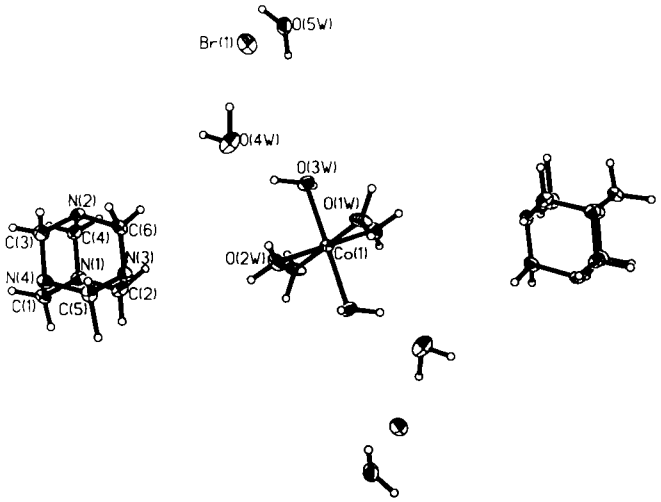


**Abstract**

$C_{12}H_{44}Br_2CoN_8O_{10}$, monoclinic, $P12_1/c1$ (No. 14), $a = 9.376(3)$ Å, $b = 18.307(5)$ Å, $c = 9.324(3)$ Å, $\beta = 118.83(1)°$, $V = 1402.1$ Å$^3$, $Z = 2$, $R_{gt}(F) = 0.064$, $wR_{ref}(F^2) = 0.178$, $T = 293$ K.

**Source of material**

To an aqueous solution of $CoBr_2$ (1.0 mmol), an ethanolic solution of hexamethylenetetramine was slowly added (2.0 mmol), the small ammount of the appreciate was dissolved by addition of few drops of dilute HBr solution. Pink block crystals were deposited after a few days.

**Discussion**

Hexamethylenetetramine (hmt) can acts not only as ligands in the preparation of the metal complexes [1-12] but also as a kind of host molecules in the formation of the inclusion compounds [13-17]. The reaction of CoX (X = halides or pesdohalides) with hmt were reported two decades ago, but few of the crystal structures of the products have been characterized [3]. We herein reported the synthesis and crystal structure of the title compound in which the hmt molecules act as the host molecules.

The structure of the title inclusion compound contains guest $[Co(H_2O)_6]^{2+}$ and $Br^-$ ions, host hmt molecules and lattice water molecules, as shown in figure. In the unit cell, the Co(II) atom, located on the 2-fold axis, is coordinated by six aqua ligands in a slightly elongated octahedron [$d$(Co—O) = 2.059 Å – 2.069 Å]. Each hmt molecule is linked to three different $[Co(H_2O)_6]^{2+}$ octahedra [$d$(N···O) = 2.697 Å – 2.841 Å], and each guest $[Co(H_2O)_6]^{2+}$ octahedron is surrounded by six different host hmt molecules through hydrogen bonds [$d$(N···O) = 2.755 Å – 2.841 Å]. It is noteworthy that many hydrogen bonds take part in the cohesion of the structure of the inclusion compound, which is closely related to thoes of $[Co(H_2O)_6]Cl_2 \cdot 2hmt \cdot 4H_2O$ [3], $[Ca(H_2O)_6]Br_2 \cdot 2hmt \cdot 4H_2O$ [9] and $[Co(H_2O)_6][NO_3]_2 \cdot 2hmt \cdot 4H_2O$ [11]. Each aqua ligand forms two donor hydrogen bonds [$d$(O1w···Br1$^i$) = 3.276 Å, $d$(O1w···N2$^{ii}$) = 2.755 Å; $d$(O2w···O5w$^{iii}$) = 2.697 Å, $d$(O2w···N1$^{iv}$) = 2.792 Å, $d$(O3w···O4w) = 2.760 Å, $d$(O3w···N4$^v$) = 2.841 Å] with hmt, lattice water molecules or $Br^-$ ions, respectively. Each of the lattice water molecules forms one receptor hydrogen bond as well as two donor hydrogen bonds [$d$(O4w···O3w) = 2.760 Å, $d$(O4w···Br1) = 3.371 Å, $d$(O4w···Br1) = 3.382 Å, $d$(O5w···O2w) = 2.697 Å, $d$(O5w···Br1) = 3.272 Å, $d$(O5w···N3$^{vi}$) = 2.801 Å] with hmt, lattice water molecules or $Br^-$ ions, respectively. Each $Br^-$ ion forms forms four receptor hydrogen bonds with one aqua ligand and three lattice molecules Br [$d$(1···O1w) = 3.276 Å, $d$(Br1···O4w) = 3.371 Å, $d$(Br1···O4w$^{vii}$) = 3.382 Å, $d$(Br1···O5w) = 3.272 Å], respectively. Symmetric codes: (*i*) $-x,-y,1-z$; (*ii*) $-x,0.5+y,0.5-z$; (*iii*) $1+x,y,z$, (*iv*) $x,0.5+y,0.5+z$; (*v*) $-1+x,0.5+y,-0.5+z$; (*vi*) $-1+x,y,z$; (*vii*) $x,-0.5-y,1-z$.

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

| | |
|---|---|
| Crystal: | pink block, size 0.36 × 0.42 × 0.46 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 35.17 cm$^{-1}$ |
| Diffractometer, scan mode: | Siemens R3m, $\omega$ |
| $2\theta_{max}$: | 53.08° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 2837, 2656 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 1725 |
| $N(param)_{refined}$: | 151 |
| Programs: | SHELXL-Plus [18], SHELXL-93 [19], ORTEP3 [20] |

**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | $x$ | $y$ | $z$ | $U_{iso}$ |
|---|---|---|---|---|---|
| H(1WA) | 4*e* | 0.0970 | 0.0961 | 0.2462 | 0.08 |
| H(1WB) | 4*e* | –0.0598 | 0.0759 | 0.2370 | 0.08 |
| H(2WA) | 4*e* | 0.2598 | –0.0933 | 0.1514 | 0.08 |
| H(2WB) | 4*e* | 0.2256 | –0.0604 | 0.2904 | 0.08 |
| H(3WA) | 4*e* | –0.1370 | –0.1129 | 0.0662 | 0.08 |
| H(3WB) | 4*e* | –0.2678 | –0.0658 | –0.1139 | 0.08 |
| H(1A) | 4*e* | 0.5233 | –0.4281 | 0.0803 | 0.08 |
| H(1B) | 4*e* | 0.4642 | –0.5070 | 0.1292 | 0.08 |

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**Table 2.** Continued.

| Atom | Site | x | y | z | $U_{iso}$ |
|---|---|---|---|---|---|
| H(2A) | 4e | 0.172 | –0.3187 | –0.0672 | 0.08 |
| H(2B) | 4e | 0.3991 | –0.3218 | –0.0090 | 0.08 |
| H(3A) | 4e | 0.3753 | –0.4954 | 0.3291 | 0.08 |
| H(3B) | 4e | 0.4049 | –0.4208 | 0.4885 | 0.08 |
| H(4A) | 4e | 0.0529 | –0.4244 | –0.0412 | 0.08 |
| H(4B) | 4e | 0.1541 | –0.5001 | 0.0195 | 0.08 |
| H(5B) | 4e | 0.5456 | –0.3192 | 0.4251 | 0.08 |

**Table 2.** Continued.

| Atom | Site | x | y | z | $U_{iso}$ |
|---|---|---|---|---|---|
| H(5A) | 4e | 0.582 | –0.3181 | 0.1944 | 0.08 |
| H(6A) | 4e | 0.1255 | –0.3155 | 0.1706 | 0.08 |
| H(6B) | 4e | 0.2514 | –0.3363 | 0.3478 | 0.08 |
| H(4WA) | 4e | –0.1524 | –0.2398 | 0.1908 | 0.08 |
| H(4WB) | 4e | –0.1586 | –0.1846 | 0.3367 | 0.08 |
| H(5WA) | 4e | –0.6527 | –0.2060 | 0.1487 | 0.08 |
| H(5WB) | 4e | –0.6008 | –0.1557 | 0.0297 | 0.08 |

**Table 3.** Atomic coordinates and displacement parameters (in $Å^2$).

| Atom | Site | x | y | z | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Co(1) | 2a | 0 | 0 | 0 | 0.0210(6) | 0.0340(7) | 0.0234(7) | –0.0012(5) | 0.0109(5) | –0.0018(5) |
| O(1W) | 4e | 0.0141(6) | 0.0664(3) | 0.1846(7) | 0.038(3) | 0.073(4) | 0.054(3) | –0.018(3) | 0.034(3) | –0.031(3) |
| O(2W) | 4e | 0.1991(6) | –0.0564(3) | 0.1732(6) | 0.036(3) | 0.061(3) | 0.027(3) | 0.020(2) | 0.014(2) | 0.012(2) |
| O(3W) | 4e | –0.1699(5) | –0.0613(3) | 0.0344(6) | 0.027(2) | 0.050(3) | 0.042(3) | –0.007(2) | 0.012(2) | 0.010(2) |
| Br(1) | 4e | –0.26021(9) | –0.16003(5) | 0.4894(1) | 0.0389(4) | 0.0598(6) | 0.0550(6) | –0.0053(4) | 0.0149(4) | –0.0143(4) |
| N(1) | 4e | 0.2991(7) | –0.4206(3) | 0.0043(6) | 0.037(3) | 0.041(3) | 0.026(3) | –0.007(3) | 0.018(3) | –0.005(2) |
| N(2) | 4e | 0.2121(7) | –0.4145(3) | 0.2103(7) | 0.036(3) | 0.044(3) | 0.033(3) | 0.006(3) | 0.024(3) | 0.012(3) |
| N(3) | 4e | 0.3429(6) | –0.3092(3) | 0.1635(7) | 0.027(3) | 0.033(3) | 0.037(3) | –0.001(2) | 0.010(2) | –0.002(3) |
| N(4) | 4e | 0.5006(6) | –0.4186(3) | 0.2907(7) | 0.024(3) | 0.050(4) | 0.031(3) | 0.000(2) | 0.011(2) | –0.001(3) |
| C(1) | 4e | 0.4585(8) | –0.4475(4) | 0.1304(9) | 0.029(3) | 0.046(4) | 0.037(4) | 0.003(3) | 0.018(3) | –0.002(3) |
| C(2) | 4e | 0.3038(9) | –0.3402(4) | 0.0027(8) | 0.039(4) | 0.044(4) | 0.036(4) | –0.007(3) | 0.019(3) | 0.002(3) |
| C(3) | 4e | 0.3736(8) | –0.4418(4) | 0.3327(8) | 0.037(4) | 0.054(5) | 0.028(4) | 0.008(3) | 0.015(3) | 0.010(3) |
| C(4) | 4e | 0.1753(8) | –0.4436(4) | 0.0515(8) | 0.024(3) | 0.041(4) | 0.033(4) | –0.005(3) | 0.009(3) | 0.004(3) |
| C(5) | 4e | 0.5008(8) | –0.3383(4) | 0.2842(8) | 0.029(3) | 0.046(4) | 0.033(4) | -0.003(3) | 0.006(3) | –0.005(3) |
| C(6) | 4e | 0.2207(8) | –0.3348(4) | 0.2071(9) | 0.031(3) | 0.049(5) | 0.047(4) | 0.010(3) | 0.022(3) | 0.007(4) |
| O(4W) | 4e | –0.1257(8) | –0.1862(4) | 0.2169(8) | 0.076(4) | 0.064(4) | 0.066(4) | –0.011(3) | 0.031(4) | 0.011(3) |
| O(5W) | 4e | –0.6073(6) | –0.1591(3) | 0.1489(6) | 0.053(3) | 0.044(3) | 0.048(3) | 0.010(2) | 0.025(3) | 0.008(2) |

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