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Crystal structure of $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$

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Hexaamminecobalt(II) bis[tetracarbonylcobaltate(-I)], $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$, was synthesized by reaction of liquid ammonia with $\text{Co}_2(\text{CO})_8$. The Co^{II} atom is coordinated by six ammine ligands. The resulting polyhedron, the hexaamminecobalt(II) cation, exhibits point group symmetry $\bar{3}$. The $\text{Co}^{-\text{I}}$ atom is coordinated by four carbonyl ligands, leading to a tetracarbonylcobaltate(-I) anion in the shape of a slightly distorted tetrahedron, with point group symmetry 3. The crystal structure is related to that of high-pressure BaC_2 (space group $R\bar{3}m$), with the $[\text{Co}(\text{NH}_3)_6]^{2+}$ cations replacing the Ba sites and the $[\text{Co}(\text{CO})_4]^-$ anions replacing the C sites. $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds between cations and anions stabilize the structural set-up in the title compound.

1. Chemical context

The reaction of $\text{Co}_2(\text{CO})_8$ with bases has already been described in the literature (Hieber *et al.*, 1960). In addition, the reaction of dicobalt octacarbonyl with liquid ammonia has been known for several decades (Behrens & Wakamatsu, 1966). Thereby $\text{Co}_2(\text{CO})_8$ forms with NH_3 hexaamminecobalt(II) bis[tetracarbonylcobaltate(-I)], $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$, which is obtained as orange air-sensitive crystals. During this reaction, CO is released and reacts with ammonia to urea. However, structural data of the title compound were missing and are presented in this communication.

2. Structural commentary

The cobalt atom Co1 of the hexaamminecobalt(II) cation occupies Wyckoff position $3a$ with site symmetry $\bar{3}$. It is coordinated by six symmetry-related ammine ligands in form of a slightly distorted octahedron. The Co–N distance in the $[\text{Co}(\text{NH}_3)_6]$ octahedron is 2.1876 (16) Å which compares well

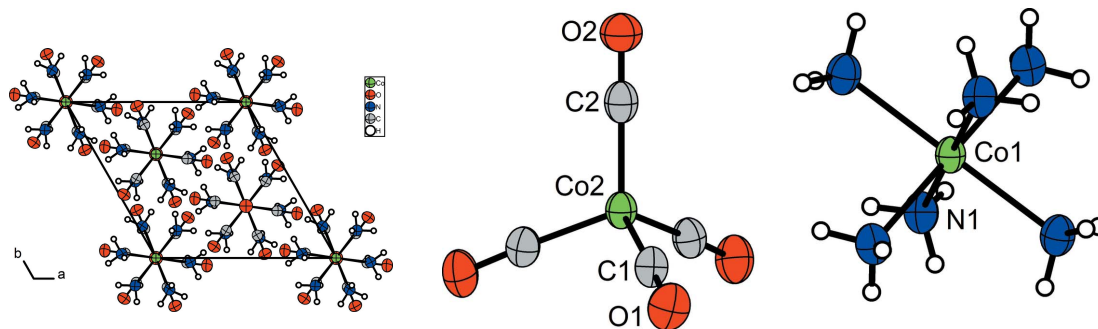


Figure 1
The molecular structures of the tetracarbonylcobaltate(-I) anion and of the hexaamminecobalt(II) cation of the title compound. Displacement ellipsoids are shown at the 70% probability level. Labelling of symmetry-equivalent atoms has been omitted for clarity.

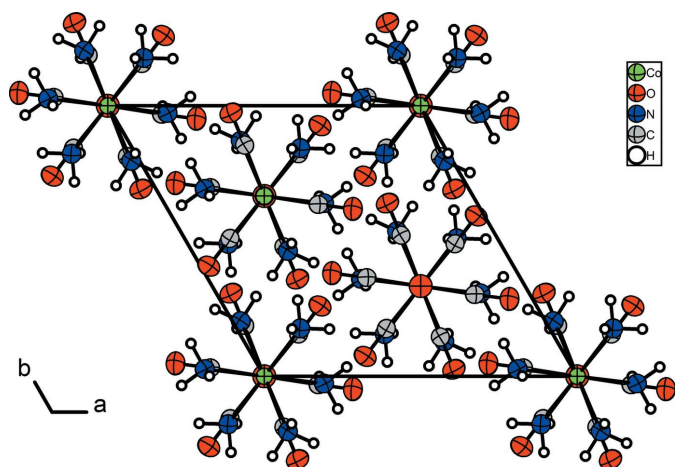


Figure 2
The unit cell of $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$, viewed along $[001]$. Displacement ellipsoids are shown at the 70% probability level.

with those of other reported hexaamminecobalt(II) structures (Barnet *et al.*, 1966).

The cobalt atom Co2 of the tetracarbonylcobaltate(–I) anion occupies Wyckoff position 6c and exhibits site symmetry 3.. It is coordinated by four carbonyl ligands in a shape close to an ideal tetrahedron. The distances between the Co2 atom and the carbon atoms C1 and C2 of the ligands are 1.7664 (18) and 1.779 (3) Å, respectively. In the literature, distances in the range from 1.77 (2) to 1.82 (2) Å are reported for Co–C in the compound $\text{Co}_2(\text{CO})_8$ (Sumner *et al.*, 1964). In the carbonyl ligands, the observed distances are in the expected range with 1.153 (2) and 1.140 (4) Å for C1–O1 and C2–O2, respectively. For the compound $\text{Co}_2(\text{CO})_8$ distances from 1.14 (2) to 1.33 (2) Å were reported (Sumner *et al.*, 1964).

The crystal structure of $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$ can be derived from the high-pressure rhombohedral phase of BaC_2 (BaC_2 -HP1, $R\bar{3}m$) (Efthimiopoulos *et al.*, 2012). Formally, the Ba sites on Wyckoff position 3a are replaced by the hexaammine cobalt(II) octahedra and the C site on position 6c is replaced by the tetracarbonylcobaltate(–I) tetrahedron.

The molecular components of the title compound are shown in Fig. 1. The unit cell of $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$ projected along $[001]$ is shown in Fig. 2.

3. Supramolecular features

The arrangement of $[\text{Co}(\text{NH}_3)_6]^{2+}$ octahedra and $[\text{Co}(\text{CO})_4]^-$ tetrahedra in the crystal structure is stabilized by N–H···O hydrogen bonds with the N1 atom as donor and the oxygen atoms O1 and O2 as acceptors atoms. One of the hydrogen bonds (N–H1C) is forked while, remarkably, in the neigh-

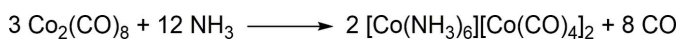


Figure 3
Reaction equation for the preparation of the title compound.

Table 1
Hydrogen-bond geometry (Å, °).

$D\text{—H}\cdots A$	$D\text{—H}$	$\text{H}\cdots A$	$D\cdots A$	$D\text{—H}\cdots A$
N1—H1A···O1 ⁱ	0.87 (4)	2.49 (4)	3.159 (2)	135 (3)
N1—H1C···O1 ⁱⁱ	0.87 (3)	2.59 (3)	3.290 (2)	138 (3)
N1—H1C···O2 ⁱⁱⁱ	0.87 (3)	2.49 (3)	3.249 (3)	146 (3)

Symmetry codes: (i) $-x + y - 1, -x - 1, z$; (ii) $x - y + \frac{2}{3}, x + \frac{1}{3}, -z + \frac{1}{3}$; (iii) $x + \frac{2}{3}, y + \frac{1}{3}, z + \frac{1}{3}$.

bourhood of the hydrogen atom H1B no acceptor atom in the range of the sum of the van der Waals radii is present. Detailed information about hydrogen-bonding distances and angles are given in Table 1.

4. Synthesis and crystallization

86 mg (29.4 mmol) of $\text{Co}_2(\text{CO})_8$ were placed in a flame-dried bomb tube under argon. 0.2 ml of liquid ammonia were condensed to the bomb tube. The bomb tube, now containing an orange solution, was flame-sealed and stored at room temperature. The reaction equation is given in Fig. 3. After six months of crystallization time, moisture- and temperature-sensitive, orange single crystals of the title compound were obtained in almost quantitative yield from the still orange solution. After manual separation of the crystals under a light-optical microscope and evaporation of the solvent only a minute orange residue remained.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$
M_r	503.07
Crystal system, space group	Trigonal, $R\bar{3}$
Temperature (K)	100
a, c (Å)	9.3679 (4), 18.3089 (18)
V (Å ³)	1391.48 (18)
Z	3
Radiation type	Mo $K\alpha$
μ (mm ^{–1})	2.70
Crystal size (mm)	0.16 × 0.12 × 0.08
Data collection	
Diffractometer	Stoe IPDS2T
Absorption correction	Integration (<i>X-RED32</i> and <i>X-SHAPE</i> ; Stoe & Cie, 2009)
$T_{\text{min}}, T_{\text{max}}$	0.649, 0.907
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7025, 994, 910
R_{int}	0.087
$(\sin \theta/\lambda)_{\text{max}}$ (Å ^{–1})	0.724
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.090, 1.08
No. of reflections	994
No. of parameters	52
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{–3})	0.87, –0.65

Computer programs: *X-AREA* (Stoe & Cie, 2011), *X-RED32* (Stoe & Cie, 2009), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Hübschle *et al.*, 2011) and *SHELXL2014* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2015) and *publCIF* (Westrip, 2010).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All hydrogen atoms of the ammine ligands were located from a difference Fourier map and were refined isotropically without any further restraints.

Acknowledgements

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Crystal structure of $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2011); cell refinement: *X-AREA* (Stoe & Cie, 2011); data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Hübschle *et al.*, 2011) and *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2015); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Hexaamminecobalt(II) bis[tetracarbonylcobaltate(-I)]

Crystal data

$[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{CO})_4]_2$
 $M_r = 503.07$
 Trigonal, $R\bar{3}$
 $a = 9.3679$ (4) Å
 $c = 18.3089$ (18) Å
 $V = 1391.48$ (18) Å³
 $Z = 3$
 $F(000) = 759$

$D_x = 1.801$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 15618 reflections
 $\theta = 3.3\text{--}33.4^\circ$
 $\mu = 2.70$ mm⁻¹
 $T = 100$ K
 Block, orange
 $0.16 \times 0.12 \times 0.08$ mm

Data collection

Stoe IPDS-2T
 diffractometer
 Radiation source: sealed X-ray tube, 12 x 0.4
 mm long-fine focus
 Plane graphite monochromator
 Detector resolution: 6.67 pixels mm⁻¹
 rotation method scans
 Absorption correction: integration
 (*X-RED32* and *X-SHAPE*; Stoe & Cie, 2009)

$T_{\min} = 0.649$, $T_{\max} = 0.907$
 7025 measured reflections
 994 independent reflections
 910 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.087$
 $\theta_{\max} = 31.0^\circ$, $\theta_{\min} = 3.3^\circ$
 $h = -13 \rightarrow 13$
 $k = -13 \rightarrow 13$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.090$
 $S = 1.08$
 994 reflections
 52 parameters
 0 restraints
 Hydrogen site location: difference Fourier map

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 1.0515P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.87$ e Å⁻³
 $\Delta\rho_{\min} = -0.64$ e Å⁻³
 Extinction correction: *SHELXL2014* (Sheldrick,
 2015), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0040 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.0000	0.0000	0.0000	0.01863 (18)
Co2	-0.6667	-0.3333	0.04221 (2)	0.01972 (17)
O1	-0.61903 (19)	-0.02591 (18)	0.10467 (9)	0.0315 (3)
O2	-0.6667	-0.3333	-0.11725 (14)	0.0298 (5)
N1	-0.0266 (2)	-0.2037 (2)	0.06820 (9)	0.0245 (3)
C1	-0.6354 (2)	-0.1451 (2)	0.07846 (10)	0.0231 (3)
C2	-0.6667	-0.3333	-0.05497 (19)	0.0237 (5)
H1A	-0.121 (5)	-0.295 (5)	0.0656 (19)	0.054 (10)*
H1B	0.034 (4)	-0.247 (4)	0.0558 (17)	0.038 (7)*
H1C	-0.001 (4)	-0.176 (4)	0.1135 (19)	0.043 (8)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0160 (2)	0.0160 (2)	0.0240 (3)	0.00799 (10)	0.000	0.000
Co2	0.01726 (19)	0.01726 (19)	0.0247 (3)	0.00863 (9)	0.000	0.000
O1	0.0323 (7)	0.0236 (7)	0.0410 (8)	0.0158 (6)	-0.0025 (6)	-0.0036 (5)
O2	0.0316 (8)	0.0316 (8)	0.0262 (12)	0.0158 (4)	0.000	0.000
N1	0.0209 (7)	0.0212 (7)	0.0307 (7)	0.0101 (6)	-0.0002 (5)	0.0015 (5)
C1	0.0192 (7)	0.0203 (7)	0.0292 (8)	0.0095 (6)	-0.0007 (6)	0.0009 (6)
C2	0.0198 (8)	0.0198 (8)	0.0317 (15)	0.0099 (4)	0.000	0.000

Geometric parameters (\AA , $^\circ$)

Co1—N1 ⁱ	2.1876 (16)	Co2—C1	1.7664 (18)
Co1—N1 ⁱⁱ	2.1876 (16)	Co2—C1 ^{vi}	1.7664 (18)
Co1—N1 ⁱⁱⁱ	2.1876 (16)	Co2—C1 ^{vii}	1.7664 (18)
Co1—N1 ^{iv}	2.1876 (16)	Co2—C2	1.779 (3)
Co1—N1	2.1877 (16)	O1—C1	1.153 (2)
Co1—N1 ^v	2.1877 (16)	O2—C2	1.140 (4)
N1 ⁱ —Co1—N1 ⁱⁱ	180.00 (9)	N1 ⁱⁱⁱ —Co1—N1 ^v	90.65 (6)
N1 ⁱ —Co1—N1 ⁱⁱⁱ	90.65 (6)	N1 ^{iv} —Co1—N1 ^v	89.35 (6)
N1 ⁱⁱ —Co1—N1 ⁱⁱⁱ	89.35 (6)	N1—Co1—N1 ^v	180.0
N1 ⁱ —Co1—N1 ^{iv}	89.35 (6)	C1—Co2—C1 ^{vi}	106.76 (7)
N1 ⁱⁱ —Co1—N1 ^{iv}	90.65 (6)	C1—Co2—C1 ^{vii}	106.75 (7)
N1 ⁱⁱⁱ —Co1—N1 ^{iv}	180.00 (11)	C1 ^{vi} —Co2—C1 ^{vii}	106.75 (7)
N1 ⁱ —Co1—N1	89.35 (6)	C1—Co2—C2	112.07 (6)
N1 ⁱⁱ —Co1—N1	90.65 (6)	C1 ^{vi} —Co2—C2	112.07 (6)

N1 ⁱⁱⁱ —Co1—N1	89.35 (6)	C1 ^{vii} —Co2—C2	112.07 (6)
N1 ^{iv} —Co1—N1	90.65 (6)	O1—C1—Co2	177.07 (17)
N1 ⁱ —Co1—N1 ^v	90.65 (6)	O2—C2—Co2	180.0
N1 ⁱⁱ —Co1—N1 ^v	89.35 (6)		

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1A...O1 ^{vii}	0.87 (4)	2.49 (4)	3.159 (2)	135 (3)
N1—H1C...O1 ^{viii}	0.87 (3)	2.59 (3)	3.290 (2)	138 (3)
N1—H1C...O2 ^{ix}	0.87 (3)	2.49 (3)	3.249 (3)	146 (3)

Symmetry codes: (vii) $-x+y-1, -x-1, z$; (viii) $x-y+2/3, x+1/3, -z+1/3$; (ix) $x+2/3, y+1/3, z+1/3$.