research communications

Crystal structure of [Co(NH$_3$)$_6$][Co(CO)$_4$]$_2$

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Hexaamminecobalt(II) bis[tetracarbonylcobaltate(-I)], [Co(NH$_3$)$_6$][Co(CO)$_4$]$_2$, was synthesized by reaction of liquid ammonia with Co$_2$(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 Co^{-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 [Co(NH$_3$)$_6$]$^{2+}$ cations replacing the Ba sites and the [Co(CO)$_4$]$^-$ anions replacing the C sites. N—H$\cdots$O hydrogen bonds between cations and anions stabilize the structural set-up in the title compound.

1. Chemical context

The reaction of Co$_2$(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 Co$_2$(CO)$_8$ forms with NH$_3$ hexaamminecobalt(II) bis[tetracarbonylcobaltate(–I)], [Co(NH$_3$)$_6$]-[Co(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 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 [Co(NH$_3$)$_6$] octahedron is 2.1876 (16) Å which compares well
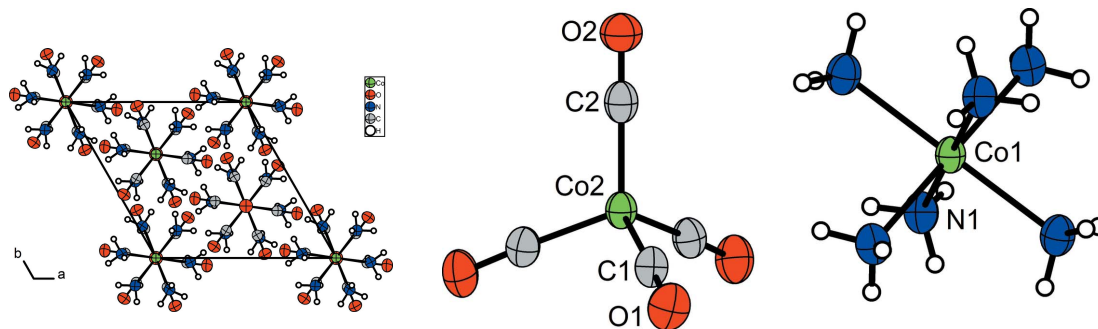

Figure 1
The molecular structures of the tetracarbonylcobaltate($-$I) anion and of the hexaamminecobalt(II) cation of the title compound. Displacement ellipsoids are shown at the 70% probability level. Labelling of symmetry-equivalent atoms has been omitted for clarity.
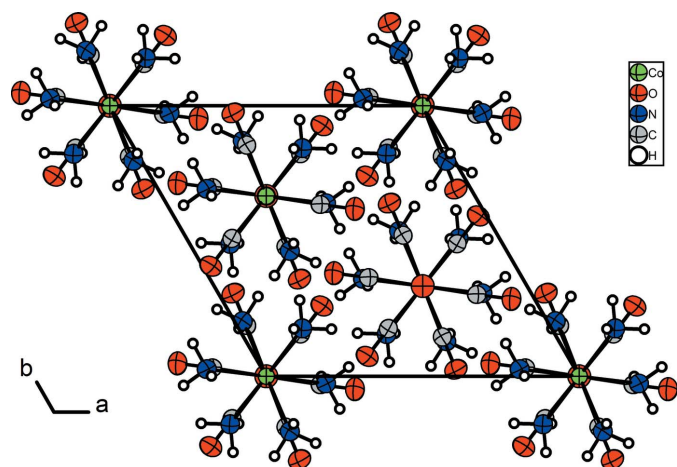
Figure 2
The unit cell of $[Co(NH_3)_6][Co(CO)_4]_2$, viewed along [001]. Displacement ellipsoids are shown at the 70% probability level.

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

The cobalt atom Co2 of the tetracarbonylcobaltate(–I) anion occupies Wyckoff position 6*c* 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 $Co_2(CO)_8$ (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 $Co_2(CO)_8$ distances from 1.14 (2) to 1.33 (2) Å were reported (Sumner *et al.*, 1964).

The crystal structure of $[Co(NH_3)_6][Co(CO)_4]_2$ can be derived from the high-pressure rhombohedral phase of BaC_2 (BaC_2 -HP1, $R\overline{3}m$) (Efthimiopoulos *et al.*, 2012). Formally, the Ba sites on Wyckoff position 3*a* are replaced by the hexaammine cobalt(II) octahedra and the C site on position 6*c* is replaced by the tetracarbonylcobaltate(–I) tetrahedron.

The molecular components of the title compound are shown in Fig. 1. The unit cell of $[Co(NH_3)_6][Co(CO)_4]_2$ projected along [001] is shown in Fig. 2.

3. Supramolecular features

The arrangement of $[Co(NH_3)_6]^{2+}$ octahedra and $[Co(CO)_4]^-$ 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-

$$3\ Co_2(CO)_8 + 12\ NH_3 \longrightarrow 2\ [Co(NH_3)_6][Co(CO)_4]_2 + 8\ CO$$

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

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

D—H···A	D—H	H···A	D···A	D—H···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 $Co_2(CO)_8$ 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	$[Co(NH_3)_6][Co(CO)_4]_2$
M_r	503.07
Crystal system, space group	Trigonal, $R\overline{3}$
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)	$0.16 \times 0.12 \times 0.08$
Data collection	
Diffractometer	Stoe IPDS2T
Absorption correction	Integration (*X-RED32* and *X-SHAPE*; Stoe & Cie, 2009)
T_{min}, T_{max}	0.649, 0.907
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7025, 994, 910
R_{int}	0.087
$(\sin \theta/\lambda)_{max}$ (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
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.87, −0.65

Computer programs: *X-AREA* (Stoe & Cie, 2011), *X-RED32* (Stoe & Cie, 2009), *SHELXT* (Sheldrick, 2015*a*), *SHELXLE* (Hübschle *et al.*, 2011) and *SHELXL2014* (Sheldrick, 2015*b*), *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.

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supporting information

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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, 2015*a*); program(s) used to refine structure: *SHELXLE* (Hübschle *et al.*, 2011) and *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *DIAMOND* (Brandenburg, 2015); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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

Crystal data

[Co(NH$_3$)$_6$][Co(CO)$_4$]$_2$	D_x = 1.801 Mg m^{-3}
M_r = 503.07	Mo $K\alpha$ radiation, λ = 0.71073 Å
Trigonal, $R\bar{3}$	Cell parameters from 15618 reflections
a = 9.3679 (4) Å	θ = 3.3–33.4°
c = 18.3089 (18) Å	μ = 2.70 mm^{-1}
V = 1391.48 (18) Å^3	T = 100 K
Z = 3	Block, orange
$F(000)$ = 759	0.16 × 0.12 × 0.08 mm

Data collection

Stoe IPDS-2T diffractometer	T_{min} = 0.649, T_{max} = 0.907
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	7025 measured reflections
	994 independent reflections
Plane graphite monochromator	910 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	R_{int} = 0.087
rotation method scans	θ_{max} = 31.0°, θ_{min} = 3.3°
Absorption correction: integration	$h = -13 \rightarrow 13$
(*X-RED32* and *X-SHAPE*; Stoe & Cie, 2009)	$k = -13 \rightarrow 13$
	$l = -26 \rightarrow 26$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0529P)^2 + 1.0515P]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.034	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.090	$\Delta\rho_{max}$ = 0.87 e Å^{-3}
S = 1.08	$\Delta\rho_{min}$ = −0.65 e Å^{-3}
994 reflections	Extinction correction: SHELXL2014
52 parameters	(Sheldrick, 2015),
0 restraints	Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Hydrogen site location: difference Fourier map	Extinction coefficient: 0.0040 (8)
All H-atom parameters refined	

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

	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 (Å, º)

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, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
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) $x+2/3$, $y+1/3$, $z+1/3$.