TU Clausthal

Structure Elucidation of $[Co(NH_3)_6][Co(CO_3)_3]$

Introduction

A green solution of tricarbonatocobaltate(III) reacts with hexaamminecobalt(III)-chloride to hexaamminecobalt(III) tricarbonatocobaltate(III) [1]. Compounds with the $[Co(CO_3)_3]$-anion are often used as an analytical titrant and as an oxidant in organic chemistry [2]. This compound is usually a very weak oxidant but when added to an acid solution the Co(III) – generated from $[Co(CO_3)_3]^{3-}$ – becomes a very strong oxidant. It is capable of reacting quantitatively with iron(II), vanadium(IV), cerium(III) and other reducing agents. Nevertheless, no x-ray single crystal data of the title compound are published, except [3].

The preparation of $[Co(NH_3)_6][Co(CO_3)_3]$ succeeded in different ways [1,4]. The structure solution of this compound can be obtained in the monoclinic space group $P2_1/c$ (No. 14) with the cell parameters a = 17.826(1), b = 10.551(1), c = 13,748(1) Å, β = 104.56(1) °, V_{EZ} = 2502.7(3) Å^3 and Z = 8.

Experimental

The title compound was prepared by adding a solution of cobalt nitrate hexahydrate to a cold potassium hydrogen carbonate solution. By adding $Co(NO_3)_2 \cdot 6\ H_2O$ and hydrogen peroxide the solution turned green. After ice cooling for one hour cobalt hexaamminechloride $Co(NH_3)_6Cl_3$ was added. The solution was allowed to stand at 6 °C. Green block shaped crystals appeared within several days.

The structure was verified by X-ray structure analysis and infrared spectroscopy.

Tab. 1 Crystallographic Data for $[Co(NH_3)_6][Co(CO_3)_3]$

Crystal system	monoclinic
Space group / Z	$P2_1/c$ (No. 14) / 8
a [Å]	17.826(1)
b [Å]	10.551(1)
c [Å]	13.748(1)
β [ ]	104.56(1)
Volume [Å^3]	2502.7(3)
D_{calc} [g · cm^{-3}]	3.160
Measurement device	STOE IPDS II
μ (MoK_α) [mm^{-1}]	2.709
F(000)	1632
T [K]	223(2)
Crystal size [mm^3]	0.26 x 0.22 x 0.24
$\Theta_{min,\ max}$ [°]	1.00 – 26.37
h_{min}, h_{max}, k_{min}, k_{max}, l_{min}, l_{max}	-21, 22, -13, 13, -17, 16
Total number of reflections	39086
Data / parameters	5082 / 493
Goodness-of-Fit	1.167
R indeces [$I>2\sigma(I)$]	$R1$ = 0.0433 ; $wR2$ = 0.0948
R indeces (all data)	$R1$ = 0.0591 ; $wR2$ = 0.0996
Largest diff. peak and hole [e Å^3]	0.673 / -0.714

Structure description

Hexaamminecobalt(III) tricarbonatocobaltate(III) crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with four formula units per unit cell and cell parameters a = 17.826(1) Å, b = 10.551(1) Å, c = 13.748(1) Å, β = 104.56(1) ° and V = 2502.7(3) Å (Tab. 1)

The crystal structure consists of four crystallographically different cobalt ions. Two cobalt ions are chelated by three carbonato groups each which are forming the anionic units $[Co(CO_3)_3]^{3-}$. The other two cobalt ions show a coordination sphere by six ammonia molecules each according to the cationic unit $[Co(NH_3)_6]^{3+}$. The NH_3-groups are involved in a hydrogen bonding network towards oxygen atoms of the carbonato groups. The corresponding bond lengths and angles are presented in the Table 2.

In Figure 1 the octahedral coordination spheres of Co2 and Co3 are shown. Those two octahedrons are connected via hydrogen bonds. The N–H···O bond lengths are in the ranges of 2.8964 – 3.0280 Å and angles of 171.49 – 172.65 °. Figure 2 shows the hydrogen bonds between Co1 and Co4. These two cobalt octahedrons are separated in the crystal structure. Only the hydrogen bond N8–H8A···O18^{i} connects them with a range of 3.070 Å.

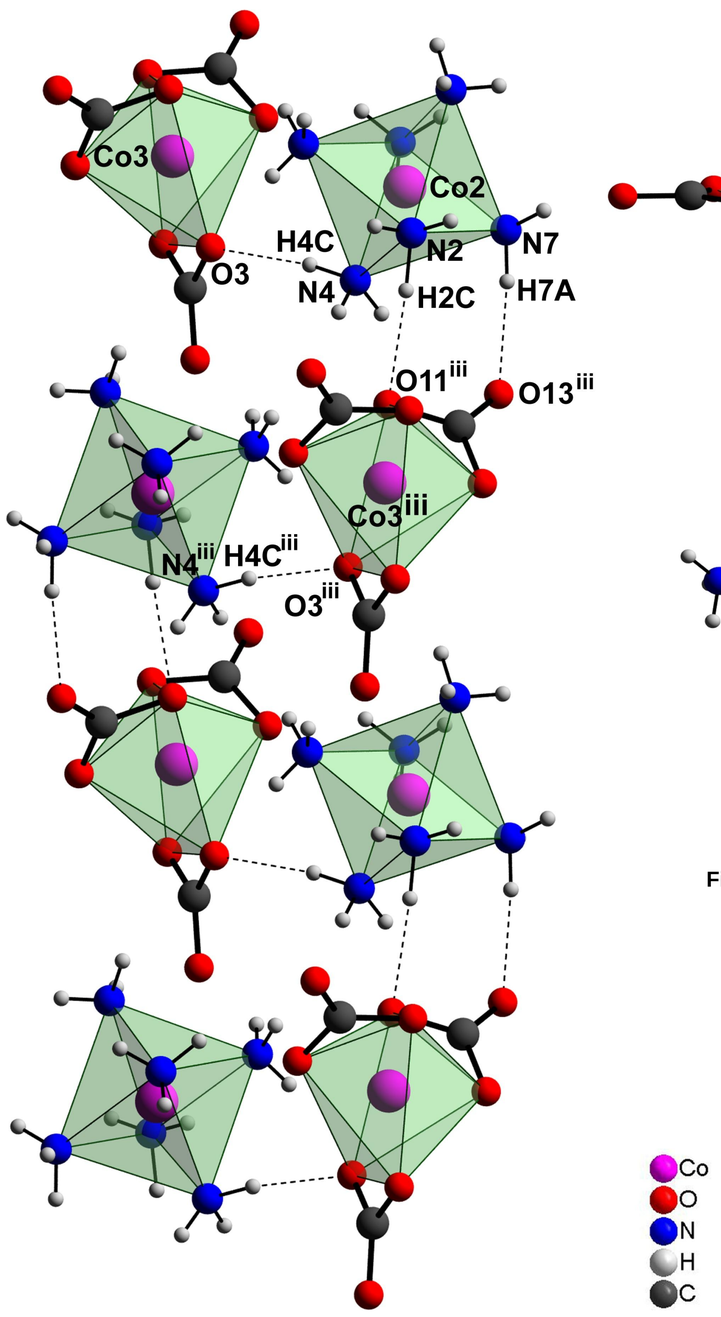

Fig. 1 Coordination sphere of Co2 and Co3 including hydrogen bonds.

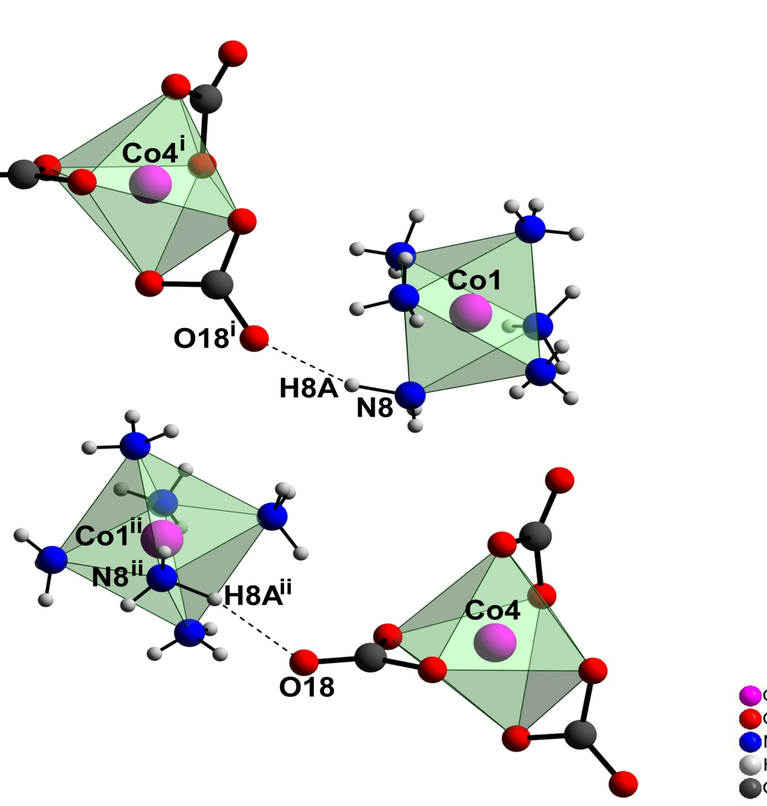

Fig. 2 Coordination sphere of Co1 and Co4 including hydrogen bonds.

Tab. 2 Bond lengths [Å] and angles [°] for $[Co(NH_3)_6][Co(CO_3)_3]$

Coordination of Cobalt			
Co1 – N(3,5,6,8,11,12)		1.945(4) – 1.976(4)	
Co2 – N(1,2,4,7,9,10)		1.942(4) – 1.975(4)	
Co3 – O(1,3,5,8,10,11)		1.904(3) – 1.924(3)	
Co4 – O(2,4,6,7,9,12)		1.907(3) – 1.929(3)	
Carbonate Groups			
C1 – $O_{(double\ bond\ character)}$	1.230(6) – 1.244(5)		
C1 – $O_{(single\ bond\ character)}$	1.302(5) – 1.323(6)		
Hydrogen bonds			
N2–H2C···O11^{iii}	3.028	∠	172.65
N4–H4C···O3	2.896	∠	171.49
N7–H7A···O13^{iii}	2.930	∠	171.77
N8–H8A···O18	3.070	∠	148.00

Symmetry codes: i) -x, y + 0,5, -z+0,5; ii) -x, y - 0,5, -z + 0,5; iii) -x + 1, y - 0,5, -z + 0,5.

Infrared spectrum

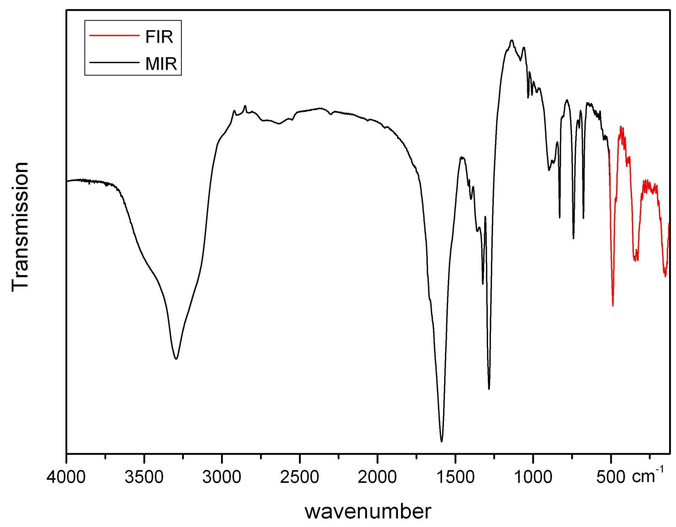

Fig. 3 Infrared spectrum of $[Co(NH_3)_6][Co(CO_3)_3]$.

In Figure 3 the infrared spectrum is shown. It is recorded by a Bruker IFS 66V using a CsI pellet.

In the range of 3600 – 3000 cm^{-1} the stretching bonds of N – H and O – H (due to intermolecular H-bonds) can be observed. The carbonate ions show the stretching bands at 1588, 1324, 1284 and 1033 cm^{-1} and the related deformation bands of the coordinated CO_3^{2-} goup in the range of 899 – 677 cm^{-1}.

The double bands at 488 and 466 respectively 344 and 327 cm^{-1} are referring to the cobalt coordination spheres (Co – N) and (Co – O).

References

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