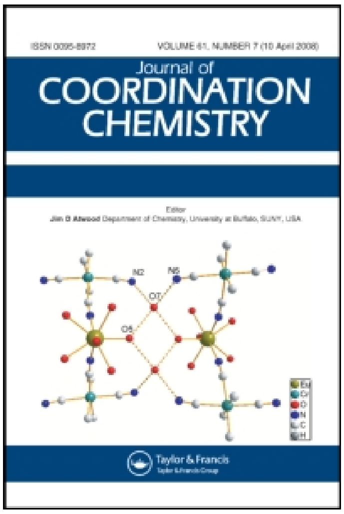

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Cationic cobaltammines as anion receptors: a convenient synthesis and the X-ray structure of hexaamminecobalt(III) chloride dichromate monohydrate

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Cationic cobaltammines as anion receptors: a convenient synthesis and the X-ray structure of hexaamminecobalt(III) chloride dichromate monohydrate

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Orange-colored single crystals of hexaamminecobalt(III) chloride dichromate monohydrate, $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$, were prepared by reacting hot aqueous solutions of hexaamminecobalt(III) chloride and potassium dichromate in a 1:1 molar ratio and allowing the mixture to cool slowly to room temperature. The salt was characterized by elemental analyses and spectroscopic studies. A single-crystal X-ray structure determination revealed that the salt crystallizes in space group $P2_1/c$ with $a = 10.0218(9)$, $b = 9.3216(8)$, $c = 16.2203(13)$ Å, $\beta = 112.962(6)°$, $V = 1395.2(2)$ Å^3, $Z = 4$ and $R = 0.0326$. In the salt, a strong network of hydrogen bonds (predominantly N–H$\cdots$O, N–H$\cdots$Cl$^-$) between the hexaamminecobalt(III) cation, the water molecule, the chloride ion and oxygen atoms of the dichromate ion represents the second sphere coordination and suggests that $[Co(NH_3)_6]^{3+}$ may be used as an anion receptor for the dichromate ion.

Keywords: Anion receptor; Cobalt(III); Dichromate ion; Second sphere coordination; Spectroscopy; X-ray structure

1. Introduction

Anions play an important role in chemistry, biology and the environment. Anion coordination chemistry – the binding of anions by receptor molecules – has been recognized and developed as a new area of chemistry [1,2]. The extraction and recovery of anions from soil and water is important if the anions are toxic [3] or have commercial values. For inorganic cations there is a wide range of extractants available because they can directly bind to ligating group on a complexant. However, capturing inorganic anions, and oxoanions in particular, is difficult because of their varied shapes, large ionic radii [4], high energy of solvation and lower Lewis basicities [5]. The design and

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synthesis of smart molecules able to function as sensors of charged species is of immense interest [6–8]. More recently, the value of weak interactions, such as C–H. . .π interactions, has been recognized [5] and the use of a few selective anion receptors for anions [9–12], such as sapphyrins [13], cationic cyclic polyamines, calixarenes, azacages or open-chain counterparts, has been reported [14]. However, these anion receptors are difficult to synthesize or are expensive. Oxoanions such as CrO_4^{2-}, PO_4^{3-}, SeO_4^{2-}, AsO_4^{3-} and $Cr_2O_7^{2-}$ are problematic contaminants in soil and water [10] because they are either toxic [15] or environmentally undesirable. Among these oxoanions the dichromate ion not only shows toxic behaviour [16] but also has a number of industrial applications [16,17]. Therefore, the search for new anion receptors [18] for dichromates that may find potential applications in analytical chemistry, biology, catalysis and waste management is important.

The hexaamminecobalt(III) cation has proven to be very useful as a large counterion in stabilizing [19] unusual pentachloro and hexachloro anions, but few studies are reported in the literature regarding complex formation of the hexaamminecobalt(III) cation with oxoanions [20,21]; e.g $[Co(NH_3)_6]Cl \cdot S_2O_3 \cdot H_2O$ and $[Co(NH_3)_6]Cl \cdot CrO_4 \cdot 3H_2O$. We have undertaken an extensive research program to explore hexaamminecobalt(III) as an anion receptor because it is relatively easy to synthesize from readily available materials and can be stored for months without decomposition. This cation meets two basic requirements for an anion receptor – high coulumbic interaction potential and hydrogen-bond donor sites. This paper reports the use of hexaamminecobalt(III) as an anion receptor for the dichromate ion. The synthesis, characterization and single-crystal X-ray structure determination of hexaamminecobalt(III) chloride dichromate monohydrate, $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$, is the continuation [22–31] of our interest in the structural chemistry of cobalt(III) complexes. We have previously reported the use of hexaamminecobalt(III) as an anion receptor for other oxoanions [29–31].

2. Experimental

2.1. *Materials*

Analytical grade reagents were used without further purification. $[Co(NH_3)_6]Cl_3$ was prepared according to the method of Bjerrum and McReynold [32].

2.2. *Instrumentation*

Cobalt and chloride were determined by standard methods [33] and C, H and N were estimated using a Perkin Elmer 2400CHN instrument. Electronic spectra were recorded using a Hitachi 330 spectrometer with water as solvent. Infrared spectra were recorded using a Perkin Elmer Spectrum RX FT-IR system using Nujol mulls between KBr plates.

2.3. *Synthesis of $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$*

Hexaamminecobalt(III) chloride (1.00 g, 0.003 mol) was dissolved in 30 cm^3 of hot water in a beaker by mechanical stirring. In another beaker 1.10 g (0.003 mol) of potassium dichromate was dissolved in 10 cm^3 of hot water. The solutions were mixed and then allowed to cool slowly; orange shiny crystals appeared within a minute and these were filtered off and dried in air. The reddish-orange colored clear supernatant solution gave a second crop of crystals. The overall yield was nearly quantitative. The complex salt decomposed at 199°C. Elemental analyses were consistent with the composition $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$ (Found: H, 6.10; N, 21.30, Cl, 8.90; Co, 14.90%; calculated: H, 6.15; N, 21.35; Cl, 9.02; Co, 14.97%).

2.4. *Crystallographic study*

Good single crystals of $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$ suitable for X-ray diffraction studies were grown from aqueous solution by slow evaporation. A single crystal with dimensions 0.1 × 0.3 × 0.4 mm was mounted along the largest dimension and used for data collection. Intensity data were collected using a Stoe Siemens AED-2 single-crystal diffractometer equipped with a sealed molybdenum tube ($\lambda = 0.71073$ Å) and a highly oriented graphite monochromator. The structure was solved by using the program SHELXTL-Plus XS [34]. All other information regarding data collection and refinement is given in table 1. Crystallographic data for the structure analysis have been deposited at the FIZ, 76344 Eggenstein-Leopoldshafen (Germany), with CSD number 413593 (tel.: (49) 7247-808-205; fax: (49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de).

Table 1. Crystal data and structure refinement details for $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$.

Empirical formula	$H_{20}ClCoCr_2N_6O_8$
Formula weight	430.6
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 10.0218(9)$ Å $b = 9.3216(8)$ Å $c = 16.2203(13)$ Å $\beta = 112.962\ (6)^\circ$
Volume	1395.2(2) $Å^3$
Z	4
Density (calculated)	2.050 $Mg\,m^{-3}$
Absorption coefficient	2.935 mm^{-1}
$F(000)$	872
Crystal size	0.1 × 0.3 × 0.4 mm
Max. and min. transmission	0.953, 0.746
θ range for data collection	2.21 to 30.00°
Limiting indices	$-13 \le h \le 1,\ -13 \le k \le 1,\ -21 \le l \le 22$
Reflections collected	5167
Independent reflections	4018 ($R_{int} = 0.0307$)
Absorption correction	Semiempirical from psi-scans
Max. and min. transmission	0.5074 and 0.3052
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4018/2/175
Goodness-of-fit on F^2 (S)	1.072
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0326,\ wR2 = 0.0906$
R indices (all data)	$R1 = 0.0373,\ wR2 = 0.0949$
Largest diff. peak and hole	0.558 and $-1.005\,e\,Å^{-3}$

3. Results and discussion

Hexaamminecobalt(III) chloride and potassium dichromate could conceivably react in a number of ways depending upon the stoichiometric ratios of reactants used. Orange-colored crystals obtained by mixing 1:1 stoichiometric quantities of hexaamminecobalt(III) chloride and potassium dichromate gave satisfactory analyses corresponding to $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$. Similar reactions were carried out with ammonium and sodium dichromate and the products obtained are identical to that obtained with potassium dichromate as indicated by color, electronic and infrared spectra. The isolated salt is not soluble in ethanol or acetone but is soluble in water, DMSO and DMF.

NH_3 stretching vibrations of the complex are lower in frequency than those of free NH_3 for two reasons; the effect of coordination and the effect of the counterions (Cl^- and $Cr_2O_7^{2-}$) in the salt. This is attributed to weakening of the N–H bond due to the formation of NH···Cl and N–H···O hydrogen bonds. For ionic $Cr_2O_7^{2-}$ there are sharp peaks [35] at 941 (Cr–O) and 756 (Cr–O–Cr) cm^{-1} as shown in table 2. Peak assignments in the IR spectrum of the title complex salt have been made in consultation with literature values [36] and are given in table 2. The electronic spectrum of the title complex salt was recorded in water. The literature [37] reports two transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, for $[Co(NH_3)_6]^{3+}$ and analogous complexes at around 470 and 340 nm, respectively, producing the familiar orange–yellow color of a number of classical coordination compounds containing cobalt(III). For the title complex salt, strong absorption maxima were observed at 360 and 260 nm. These bands in comparison with electronic spectrum of $K_2Cr_2O_7$ in water, i.e. maxima at 351 and 256 nm, are attributed to the dichromate ion. The hexaamminecobalt(III) cation does not show the peak $^1A_{1g} \rightarrow {}^1T_{2g}$ because of overlapping of charge transfer bands of the dichromate ion; a shoulder at 460 nm corresponds to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition.

3.1. *X-ray crystallography*

The structure of the title complex salts has been unambiguously determined by single-crystal X-ray crystallography and reveals the presence of discrete $[Co(NH_3)_6]^{3+}$, Cl^- and $Cr_2O_7^{2-}$ ions and one molecule of water in the lattice. The atom numbering scheme and structure are shown in figure 1. A special feature is the presence of a "sandwiched" water molecule between the hexaamminecobalt(III) cation and the dichromate anion. In $[Co(NH_3)_6]^{3+}$, the cobalt(III) ion possesses nearly regular

Table 2. Infrared data for salts containing the $[Co(NH_3)_6]^{3+}$ cation.

Infrared frequencies (cm^{-1}) $[Co(NH_3)_6]Cl_3$	$[Co(NH_3)_6]Cl \cdot Cr_2O_7 \cdot H_2O$	Assignment
	3447	ν(O–H)
3240	3258	ν_{as}(N–H)
3160	3140	ν_s(N–H)
1619	1615	δ_d(N–H)
1326	1336	δ_s(N–H)
	941	ν(Cr–O)
831	830	ρ_r(N–H)
	756	ν(Cr–O–Cr)

Table 3. Selected bond lengths [Å] and angles [°] for $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$.

Co–N(1)	1.971(2)	Cr(1)–O(1)	1.799(2)
Co–N(2)	1.977(2)	Cr(1)–O(2)	1.612(2)
Co–N(3)	1.964(2)	Cr(1)–O(3)	1.605(2)
Co–N(4)	1.964(2)	Cr(1)–O(4)	1.609(2)
Co–N(5)	1.954(2)	Cr(2)–O(1)	1.767(2)
Co–N(6)	1.958(2)	Cr(2)–O(5)	1.624(2)
		Cr(2)–O(6)	1.626(2)
		Cr(2)–O(7)	1.614(2)
N(1)–Co–N(2)	91.67(7)	O–(1)–Cr(1)–O(2)	108.05(9)
N(1)–Co–N(3)	88.82(8)	O–(1)–Cr(1)–O(3)	108.68(9)
N(1)–Co–N(4)	89.17(7)	O–(1)–Cr(1)–O(4)	109.61(10)
N(1)–Co–N(5)	178.72(7)	O–(2)–Cr(1)–O(3)	110.96(11)
N(1)–Co–N(6)	90.76(8)	O–(2)–Cr(1)–O(4)	109.25(12)
N(2)–Co–N(3)	91.18(7)	O–(3)–Cr(1)–O(4)	110.26(13)
N(2)–Co–N(4)	178.88(7)	O–(1)–Cr(2)–O(5)	106.65(8)
N(2)–Co–N(5)	89.10(7)	O–(1)–Cr(2)–O(6)	107.54(8)
N(2)–Co–N(6)	89.64(7)	O–(1)–Cr(2)–O(7)	110.49(11)
N(3)–Co–N(4)	89.97(7)	O–(5)–Cr(2)–O(6)	109.93(9)
N(3)–Co–N(5)	90.10(8)	O–(5)–Cr(2)–O(7)	110.74(9)
N(3)–Co–N(6)	178.78(7)	O–(6)–Cr(2)–O(7)	111.34(9)
N(4)–Co–N(5)	90.14(7)	O–(2)–O(1)–O(1)	124.86(9)
N(4)–Co–N(6)	89.21(8)		
N(5)–Co–N(6)	90.31(9)		

octahedral geometry. N–H bond distances are in the range 1.954(2)–1.977(2) Å, while *cis* N–Co–N bond angles are in the range 88.82(8)–91.61(7)° and *trans* N–Co–N bond angles are in the range 178.72(7)–178.88(7)°. Selected bond angles and lengths are listed in table 3. In hexaamminecobalt(III) chloride [38], the average Co–N distance is 1.963 Å and the maximum deviation of *cis* N–Co–N bond angles from their ideal values is 2.1°, with a standard deviation of 0.7°. Structural parameters of the present cation are also in agreement with the earlier reported structures of hexaamminecobalt(III) chloride selenate trihydrate [29] and hexaamminecobalt(III) chloride dimethanesulfonate [30].

The dichromate anion ($Cr_2O_7^{2-}$) has two bonding modes with metal or ammonium ions, ionic [39–43] and bidentate [44,45] (bridging). The dichromate ion in the present complex salt is ionic. The average Cr–O^b (bridging) distance is 1.703(2) Å and Cr–O^t (terminal) distances range from 1.605(2) to 1.626(2) Å (figure 1). The bond angles ∠O^b–Cr–O^t are within the normal tetrahedral range [108.05(9)–110.74(9)°] and the bridging angle ∠Cr–O^b–Cr is 124.86(9)°.

The $[Co(NH_3)_6]^{3+}$, Cl^-, $Cr_2O_7{}^{2-}$ ions and water molecule are held together by electrostatic forces and hydrogen bonding of the type O–H···O, N–H···Cl^- and O–H···Cl^-, resulting in a three-dimensional hydrogen-bonded network through the second sphere coordination (figure 1), similar to that present in $[Co(NH_3)_6]Cl(CH_3SO_3)_2$ [30]. The X-ray structure determination of $[Co(NH_3)_6]Cl(CH_3SO_3)_2$ revealed an interesting network of N–H···O and N–H···Cl^- hydrogen bonds that serve to stabilize layers in the lattice. Thus it may be possible to achieve a range of molecular organization through second sphere coordination involving hydrogen bonds in these kinds of complexes. Possible hydrogen bonds in $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$ are given in table 4. The formation of a complex salt of definite composition $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$ when hexaamminecobalt(III) chloride and potassium dichromate are reacted in a

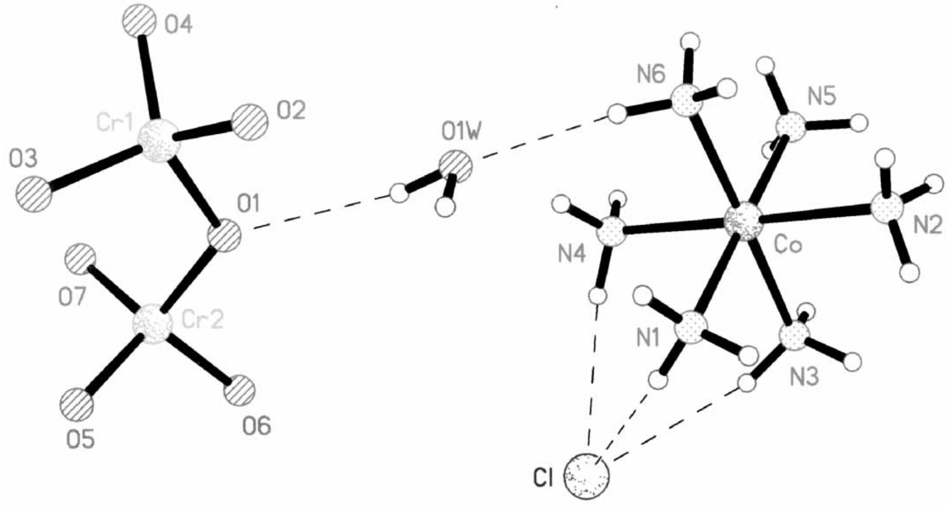

Figure 1. Ball-and-stick diagram of $[Co(NH_3)_6]ClCr_2O_7.H_2O$ showing the atom numbering scheme and second sphere coordination via hydrogen bonding.

Table 4. Possible hydrogen bond lengths [Å] for $[Co(NH_3)_6]ClCr_2O_7 \cdot H_2O$.

N(1)–O(5)$^{\#1}$	3.031(2)
N(1)–Cl	3.354(2)
N(3)–O(6)$^{\#1}$	3.022(2)
N(3)–Cl$^{\#1}$	3.310(2)
N(3)–Cl	3.320(2)
N(4)–Cl	3.267(2)
N(5)–O(2)$^{\#2}$	2.908(2)
N(5)–O(6)$^{\#3}$	3.031(2)
N(5)–O(2)$^{\#4}$	3.032(3)
N(6)–O(1W)	2.964(3)
O(1W)–O(1)	2.944(2)
O(1W)–Cl$^{\#5}$	3.168(2)

Operators for generating equivalent atoms: $^{\#1}-x+1,\ y-1/2,\ -z+1/2$; $^{\#2}x,\ y-1,\ z$; $^{\#3}x,\ -y+1/2,\ z-1/2$; $^{\#4}-x,\ -y+1,\ -z$; $^{\#5}-x+1,\ y+1/2,\ -z+1/2$.

1:1 molar ratio in aqueous media shows that $[Co(NH_3)_6]^{3+}$ may find application as a receptor for the toxic and commercially important dichromate ion.

Acknowledgments

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