Inorganica Chimica Acta, 182 (1991) 135–138

Properties and structure of the cobalt(III) chromate cation, $Co(NH_3)_5CrO_4{}^+$, as its perchlorate salt

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(Received October 8, 1990)

Abstract

The reaction between $Co(NH_3)_5OH_2{}^{3+}$ and $CrO_4{}^{2-}$ at pH 6.5 in aqueous solution produces $[Co(NH_3)_5CrO_4](ClO_4)$, which has been characterized by a single crystal X-ray diffraction study. Brown crystals of the complex are orthorhombic, with space group $Cmc2_1$ and lattice constants $a=10.120(3)$, $b=12.431(3)$, $c=8.591(1)$ Å and $Z=4$. The structure consists of discrete $Co(NH_3)_5CrO_4{}^+$ and $ClO_4{}^-$ ions, each of which is centred on a mirror plane such that asymmetric repeat unit is comprised of half the formula unit. The cation may be considered as a cobalt(III) octahedral environment linked to a tetrahedrally coordinated chromium (VI) centre through a common oxygen atom. Deviations from idealized Co(III) octahedral geometry arise from steric effects and significant intra- and intermolecular hydrogen bonding.

Introduction

As part of a study into the substitution mechanisms of aqueous oxo anions [1], we have directed attention to the isolation of the product of the reaction between $Co(NH_3)_5OH_2{}^{3+}$ and $CrO_4{}^{2-}$. The first preparation of a metal complex containing a chromate ligand was reported by Briggs [2], who synthesized a series of cobalt(III) chromato ammine salts by reacting K_2CrO_4 with the corresponding cobalt(III) aquoammine complex. Several subsequent studies have focussed on magnetic properties and infrared examination of the $CrO_4{}^{2-}$ coordination mode in Co(III) and Cr(III) ammine chromato complexes [3–6], although no structural characterization by X-ray diffraction has been reported. We detail here the synthesis, magnetic properties, characterization and X-ray structure of $[Co(NH_3)_5CrO_4](ClO_4)$.

Discussion

Characterization

Electron microprobe, NH_3 and $CrO_4{}^{2-}$ analyses confirm the stoichiometry of the compound to be consistent with the formulation, $Co(NH_3)_5CrO_4ClO_4$.

Coomber and Griffith [5] have utilized the ν_1 symmetric mode of $CrO_4{}^{2-}$ to distinguish between the structural isomers $[Co(NH_3)_5CrO_4]Cl$ (875 cm^{-1}) and $[Co(NH_3)_5Cl](CrO_4)$ (847 cm^{-1}, where ν_1 for free $CrO_4{}^{2-}$ is also 847 cm^{-1}). Casabo *et al.* reported ν_1 frequencies of 870 cm^{-1} for $Cr(NH_3)_5CrO_4{}^+$ and 890 cm^{-1} for the bidentate $CrO_4{}^{2-}$ in $Cr(NH_3)_4CrO_4{}^+$ [6]. The strong ν_1 stretch at 872 cm^{-1} for $[Co(NH_3)_5CrO_4](ClO_4)$ is indicative of a monodentate chromate ligand bound to the Co(III). The similarity in the strong ν_4 $ClO_4{}^-$ frequencies between free $ClO_4{}^-$ (625 cm^{-1}) [7] and the title complex (627 cm^{-1}) suggests retention of the perchlorate T_d symmetry, which therefore remains noncoordinated.

At 298 K, the effective magnetic moment, μ_{eff}, of $[Co(NH_3)_5CrO_4](ClO_4)$ was found to be 0.62 BM which is consistent with the results for many other low-spin Co(III) compounds which have moments over the range 0 to 1 BM [8, 9]. The Co(III) d^6 ion is expected to be diamagnetic and positive values for μ_{eff} are explained in terms of temperature independent paramagnetism, where there is a coupling of the ground state with excited states induced by the applied field. This phenomenon is illustrated by the invariant value of the molar susceptibility ($2.18 \pm 0.06 \times 10^{-9}$ m^3 mol^{-1}) over a temperature range of 200–330 K. The $CrO_4{}^{2-}$ ligand would be expected to also make a small contribution to μ_{eff} since Na_2CrO_4 has a corrected magnetic moment of 0.15 BM [8] due to temperature independent paramagnetism.

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0020-1693/91/$3.50

Structural studies

Fractional atomic coordinates and equivalent isotropic thermal parameters from the single crystal X-ray diffraction study of $[Co(NH_3)_5CrO_4](ClO_4)$ are given in Table 1. Selected bond lengths and angles are presented in Table 2 and the geometry of the cation is illustrated in Fig. 1*. The structure consists of discrete $Co(NH_3)_5CrO_4^+$ and ClO_4^- ions with a mirror plane passing through atoms H(1,1), N(1), Co, O(1), Cr and O(3) of the cation and continuing through O(4), Cl and O(5) of the perchlorate; resulting in the asymmetric unit comprising half the formula unit. A common oxygen atom, O(1), bridges the octahedral Co(III) and the tetrahedrally coordinated Cr(VI).

The average Co–N bond length of 1.95 Å is typical of the values found in many other cobalt(III) ammine complexes [10–12]. The Co–N(1) distance of 1.948(9) Å is intermediate between the two other unique Co–N bond lengths (Co–N(2) 1.943(7) and Co–N(3) 1.960(7) Å, indicating that there is no discernible *trans* effect in this complex.

The Co–O(1)–Cr angle of 134.3(4)° is much larger than the 123° Cr–O–Cr bridge in the dichromate anion, $Cr_2O_7^{2-}$ [13]. This suggests that steric effects make a significant contribution to the stereochemistry of the $Co(NH_3)_5CrO_4^+$ cation. The intramolecular contact distance of 3.103(8)·Å between N(3) and O(2$^{\mathrm{I}}$) is only marginally greater than the sum of the van der Waal's radii (3.07 Å [14]). Any further closing of the bridging angle would cause unfavourable repulsion between these atoms. A similar intramolecular N–O contact of 3.08(4) Å in the polymeric $Zn(NH_3)_2(CrO_4)_2^{2-}$ anion may also be

TABLE 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for $[Co(NH_3)_5CrO_4](ClO_4)$

Atom	x	y	z	U_{eq}^{a}
Co	0.0000	0.6248(1)	0.5000	0.0139(5)
Cr	0.0000	0.3559(1)	0.5160(2)	0.0178(8)
Cl	0.5000	0.4555(2)	0.6879(3)	0.025(1)
N(1)	0.0000	0.7679(7)	0.4216(9)	0.022(4)
H(1,1)	0.0000	0.762(9)	0.327(11)	0.04(2)^{b}
H(1,2)	0.071(9)	0.808(5)	0.436(8)	0.04(2)
O(1)	0.0000	0.4839(4)	0.5778(7)	0.020(3)
N(2)	−0.1628(7)	0.6634(5)	0.6245(7)	0.027(3)
H(2,1)	−0.226(8)	0.706(6)	0.612(9)	0.04(1)
H(2,2)	−0.204(9)	0.609(6)	0.640(8)	0.04(1)
H(2,3)	−0.147(9)	0.682(6)	0.699(9)	0.04(1)
N(3)	−0.1635(7)	0.5815(5)	0.3758(7)	0.031(3)
H(3,1)	−0.150(8)	0.585(6)	0.280(9)	0.04(1)
H(3,2)	−0.194(10)	0.524(6)	0.379(8)	0.04(1)
H(3,3)	−0.249(9)	0.639(6)	0.385(7)	0.04(1)
O(2)	0.1547(6)	0.3353(4)	0.4257(5)	0.033(3)
O(3)	0.0000	0.2757(5)	0.6417(8)	0.039(5)
O(4)	0.5000	0.5418(7)	0.7772(11)	0.064(7)
O(5)	0.5000	0.3583(6)	0.7656(17)	0.070(7)
O(6)	0.6362(6)	0.4549(6)	0.6094(6)	0.064(5)

^{a}$U_{eq}=\frac{1}{3}(U_{11}+U_{22}+U_{33})$. ^{b}All hydrogen atoms were refined isotropically ($U_{eq}=U_{iso}$).

TABLE 2. Selected bond lengths and angles for $[Co(NH_3)_5CrO_4](ClO_4)$

Atoms	Bond length (Å)	Atoms	Bond angle (°)
Co–N(1)	1.948(9)	N(1)–Co–N(2)	92.2(3)
Co–N(2)	1.943(7)	N(1)–Co–N(3)	89.4(3)
Co–N(3)	1.960(7)	N(2)–Co–N(2$^{\mathrm{I}}$)	92.1(3)
Co–O(1)	1.920(6)	N(3)–Co–N(3$^{\mathrm{I}}$)	91.5(3)
Cr–O(1)	1.710(6)	N(2)–Co–N(3)	88.2(3)
Cr–O(2)	1.633(5)	N(1)–Co–O(1)	179.8(3)
Cr–O(3)	1.616(8)	N(2)–Co–O(1)	87.7(2)
Cl–O(4)	1.403(10)	N(3)–Co–O(1)	90.7(2)
Cl–O(5)	1.442(12)	Co–O(1)–Cr	134.3(4)
Cl–O(6)	1.414(6)	O(1)–Cr–O(2)	110.5(2)
		O(1)–Cr–O(3)	106.6(4)
		O(2)–Cr–O(2$^{\mathrm{I}}$)	108.9(3)
		O(2)–Cr–O(3)	110.1(2)

Symmetry operations: I: $-x, y, z$; II: $-x, 1-y, 0.5+z$; III: $x, 1-y, 0.5+z$; IV: $-1+x, y, z$; V: $-x, 1-y, -0.5+z$; VI: $0.5-x, 1.5-y, 0.5+z$; VII: $0.5-x, -0.5+y, z$.

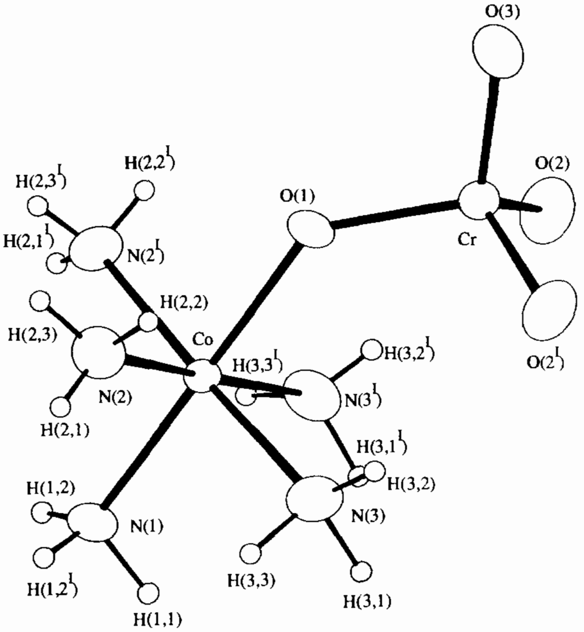

Fig. 1. Structure of the $Co(NH_3)_5CrO_4^+$ cation.

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*The superscripted Roman numerals appearing in the text, diagrams and tables refer to the symmetry transformations listed in Table 2.

TABLE 3. Hydrogen bonding contact distances (<2.5 Å) for $[Co(NH_3)_5CrO_4](ClO_4)$[a]

Contact	Distance (Å)	Contact	Distance (Å)
$O(1)\cdots H(2,2)$	2.43(8)	$H(3,2)\cdots O(2^{I})$	2.42(7)
$O(3)\cdots H(1,1^{II})$	1.94(11)	$O(5)\cdots H(3,3^{II})$	2.47(8)
$H(2,2)\cdots O(6^{IV})$	2.38(7)	$O(2)\cdots H(2,3^{V})$	2.31(9)
$O(4)\cdots H(1,1^{VI})$	2.49(11)	$O(2)\cdots H(1,2^{VII})$	2.39(8)

[a] The superscripted Raman numerals refer to the symmetry operations listed in Table 2.

predominantly responsible for the Zn–O–Cr bridge angle of 134(1)° [15].

Intra- and intermolecular hydrogen bonding also exert significant influences on the structure, with contacts less than 2.5 Å listed in Table 3. Intramolecular (N)–H···O distances of 2.42(7) and 2.43(8) Å have been found between the ammine ligands on the cobalt and the terminal chromate oxygen, O(2) and the bridging oxygen, O(1), respectively. There is an especially strong intercationic hydrogen bond of 1.94(11) Å between H(1,1) on N(1) and $O(3^{II})$. Gatehouse and Guddat report similar strong, hydrogen bonding (N)–H···O distances of 1.92(3) and 1.94(2) Å in the infinite chain anion, $Cu(NH_3)_2(CrO_4)_2^{2-}$ [16]. A further intermolecular (N)–H···O contact of 2.31(9) Å was found between $O(2^{II})$ and H(2,3) on N(2) in $Co(NH_3)_5CrO_4^+$. Cation units lie 'head to tail' to maximize these interactions. There is also moderate hydrogen bonding between the cation and the perchlorate counter ion, with observed contacts between 2.38(7) and 2.49(11) Å.

Analysis of mean planes data shows that the cobalt ion lies out of the plane formed by N(2), N(3), $N(2^{I})$ and $N(3^{I})$ by 0.028 (1) Å in the direction of N(1). This small effect may arise from the nitrogen atoms N(2) and $N(2^{I})$ being drawn towards the bridging oxygen, O(1) and also possibly towards $O(2^{II})$ and $O(2^{III})$ on the neighbouring chromate group, to facilitate hydrogen bonding interactions. The N(2)–Co–O(1) angle of 87.7(2)° supports this contention.

Experimental

Crystals of $[Co(NH_3)_5CrO_4](ClO_4)$ were grown according to the method of Briggs [2] (the counter ion was changed from NO_3^- to ClO_4^-). Air stable, brown crystals suitable for structural determination were obtained from slow second-crop evaporation of the mother liquor. $[Co(NH_3)_5OH_2](ClO_4)_3$ was prepared by acidification of $[Co(NH_3)_5CO_3](NO_3)$ [17] and recrystallized from 0.01 M $HClO_4$. $Na_2CrO_4 \cdot 2H_2O$ was obtained upon cooling a solution of $Na_2Cr_2O_7 \cdot 2H_2O$ and NaOH (pH 11–12) and recrystallized from base solution.

Analysis of NH_3 content was performed using an adaptation of the method described by Vogel [18]. The complex was dissolved in 0.5 M NaOH and heated until decomposition was complete (*c.* 1 h). Liberated NH_3 was carried by nitrogen into a Dreschel bottle containing boric acid. $H_2BO_3^-$ was titrated against HCl. Calc. for $[Co(NH_3)_5CrO_4](ClO_4)$: 23.68, found 23.49%. CrO_4^{2-} was obtained by filtering off the insoluble, black Co(III) hydroxides and determined spectrophotometrically at 380 nm ($\epsilon = 4636$ M^{-1} cm^{-1} [1]). Found 32.09, calc. 32.26%.

Electron microprobe analysis was performed using a Jeol JSM-840A scanning electron microscope. Analysis showed a homogeneous solid with constant composition. The experimentally determined elements and their ratios were Co:Cr:Cl = 1:1:1 in agreement with the postulated formula.

Infrared spectra were recorded as KBr discs on a Jasco 302 infrared spectrometer. Variable temperature magnetochemical measurements were performed on a thermostatted Gouy balance, calibrated with $Hg[Co(NCS)_4]$. Diamagnetic corrections were applied according to König [8].

Structural determination

Crystals of $H_{15}ClCoCrN_5O_8$ are *C*-centred orthorhombic, $M = 395.5$, $a = 10.120(3)$, $b = 12.431(2)$, $c = 8.591(1)$ Å, $U = 1080.7(6)$ $Å^3$, $D_m = 2.20$ Mg m^{-3} (measured by flotation in CH_3CH_2I/CH_2Br_2), $Z = 4$, $D_c = 2.21$ Mg m^{-3}, $F(000) = 728$, space group $Cmc2_1$ (No. 36), $\mu = 27.53$ cm^{-1}, $T = 293(1)$ K.

Intensity data were collected at room temperature using an Enraf-Nonius CAD-4F diffractometer, fitted with graphite monochromatized Mo Kα radiation, 0.71069 Å. A preliminary scan revealed systematic absences which were consistent with the space groups *Cmcm* (No. 63), *C2cm* (No. 40, non-standard setting of *Ama*2) and $Cmc2_1$ (No. 36). The ω:2θ scan technique was employed to measure 1634 reflections to a maximum Bragg angle of 27.5° in the range $-11 \leqslant h \leqslant 11$, $-1 \leqslant k \leqslant 16$, $-1 \leqslant l \leqslant 13$. Of the 768 unique reflections, 652 satisfied the $I \geqslant 2\sigma(I)$ criterion and were used in subsequent analysis. No crystal decomposition occurred during the data collection. Corrections were applied for Lorentz and polarization effects and for absorption [19].

The structure was solved by a combination of direct methods and Patterson synthesis [20] and refined using a full matrix least-squares procedure which minimized the function $\Sigma w \Delta^2$, where $\Delta = \| F_o | - | F_c \|$ and w was the weight applied to each reflection [19]. The z coordinate of all atoms was referenced to that of the cobalt atom, which was fixed at 0.5. Of the three possible space groups, only $Cmc2_1$ yielded a satisfactory solution.

All hydrogen atoms were located from difference maps and their positions refined. Common isotropic temperature factors were applied to hydrogen atoms of each ammine ligand. Anisotropic thermal parameters were applied to all other atoms. A weighting scheme of the form $w = k/(\sigma^2(F) + gF^2)$ was included in each refinement cycle. At convergence, the values of k, g, R and R_w were 0.9912, 0.00040, 0.030 and 0.029, respectively. In order to establish the absolute configuration of the structure, an identical refinement procedure was carried out using the inverse set of coordinates. Refinement in the other enantiomorph gave significantly higher R and R_w values (0.034 and 0.035), indicating that the original enantiomorph was the correct configuration.

Scattering factors for H, N, O and Cl were incorporated into the SHELX-76 program [19], whilst those for Co and Cr (corrected for anomalous dispersion) were taken from ref. 21. Calculations were performed on VAX 11/8650 and 11/780 computer systems. The diagram was drawn using the ORTEP program [22].

Supplementary material

Listings of thermal parameters, bond distances and angles, mean planes data, observed and calculated structure factors and temperature dependent magnetic measurements are available from author P.A.T. on request.

Acknowledgement

M.R.G. is grateful to the Australian Government for a Commonwealth Postgraduate Research Award.

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