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Structure and Bonding of $[Cr(H_2O)_5NO]SO_4$

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The crystal structure of $[Cr(H_2O)_5NO]SO_4$ has been determined. The complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.058(3)$ Å, $b = 6.846(1)$ Å, $c = 11.382(3)$ Å, $\beta = 110.14(2)°$, $Z = 4$, and R (R_w) = 0.033 (0.045) for 1854 reflections with $I \geq 3\sigma(I)$. The structural data are incompatible with an oxidation state of +1, which has previously been assigned to the chromium atom, and support the formulation of this compound as a chromium(III) complex of NO^-. A new preparative method of the title compound is reported.

Introduction

After its synthesis[1] was first reported, a wide range of formation and decomposition reactions of $[Cr(H_2O)_5NO]^{2+}$ were investigated. These included thermal, photochemical, and electrochemical reactions, redox as well as substitution reactions.[2–15] This ion was first characterized as a complex of chromium(III) with an NO^- ligand.[1] Its chemical properties are, indeed, characteristic of a chromium(III) complex: its rate of aquation is slow, as are other substitution reactions,[1,6,7] and its high $pK_a = 4.8$[15] corresponds to those of other $[Cr^{III}(H_2O)_5X]^{2+}$ ions.

An alternative formulation of this complex, $[Cr^INO(H_2O)_5]^{2+}$, i.e. a chromium(I) coordinated to an NO^+ ligand,[2] was based on the observed N–O stretching frequency ($\nu = 1747$ cm^{-1}) and the magnetic moment ($\mu = 2.2\ \mu_B$). This formulation has been accepted,[15] in spite of the chemical properties, which are typical for a Cr(III) complex.

During the seventies and eighties it was realized that the N–O stretching frequencies and magnetic moments in related complexes such as $[Cr(CN)_5NO]^{3-}$ were not reliable tools for assigning oxidation states to the chromium and nitrogen atoms.[16,17] The single-crystal X-ray study of $[Cr(H_2O)_5NO]SO_4$, reported here, was undertaken in order to obtain reliable structural data which might be relevant to the problem of structure and bonding of this complex. This is the first single-crystal X-ray study ever done on an $[M(H_2O)_5NO]^{n+}$ compound. The instability of the famous "brown ring" complex $[Fe(H_2O)_5NO]^{2+}$ imposes difficulties on eventual X-ray studies of its salts.

Experimental Section

Compound Preparation. Two methods were used for preparation of $[Cr(H_2O)_5NO]SO_4$: (a) As previously reported[1] by reacting $Cr(ClO_4)_2$ with NO; (b) by reduction of chromic acid with hydroxylammonium chloride. In method b, 3 g of CrO_3 was dissolved in 100 mL of water, and the solution was added dropwise to a stirred solution of 4 g of NH_3OHCl dissolved in 100 mL of water. Argon was passed through the solution for 30 min to remove nitrogen oxides. The resulting deep brown solution, containing $[Cr(H_2O)_5NO]^{2+}$ together with large quantities of the chromic hexaaqua ion and "chromic dimer", was absorbed on a Dowex 50X2 (100–200 mesh) cation-exchange column. Absorption was continued until the column was completely loaded with chromic species and the red-brown solution of (impure) $[Cr(H_2O)_5NO]^{2+}$ came off the column. This solution was reabsorbed on a second ion-exchange column and eluted with 0.5 M H_2SO_4. The most concentrated fraction was placed in a small Petri dish and concentrated by evaporation at room temperature. Red brown crystals (plates) were formed overnight and were washed with acetone and dried.

Physical Measurements. The magnetic susceptibility of a powdered sample of $[Cr(H_2O)_5NO]SO_4$ was measured by the Gouy method at 19 °C. Found: $\mu_{eff} = 2.02\ \mu_B$. The infrared spectrum of the compound, using a KBr disk, was measured on a Bruker IFS 113V interferometer. The sharp band of N–O stretching was recorded at 1733 cm^{-1}. Strong stretching and bending bands of SO_4^- at 1056 cm^{-1} and around 600 cm^{-1}, respectively, were also recorded, as were stretching bands of the H_2O ligand around 3300 cm^{-1} and the bending band at 1653 cm^{-1}.

X-ray Crystallography. Data were measured on a PW1100/20 Philips four-circle diffractometer using graphite-monochromated Mo Kα radiation. The unit cell parameters were obtained by a least-squares fit of 24 reflections with $\theta = 12$–$15°$. Intensity data were collected using the ω–2θ technique to a maximum 2θ of 60°. The scan width, $\Delta\omega$, for each reflection was $1.00 + 0.35 \tan\theta$ with a constant speed of 3.0°/min. Background measurements were made for 10 s at each limit of a scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Intensities were corrected for Lorenz and polarization effects. All non-hydrogen atoms were found by using the results of the SHELXS-86 direct method analysis.[18] After a few cycles of refinement,[19] the hydrogen atoms were located in a difference Fourier map and their positions were fixed in the subsequent cycles of refinement. Finally, a correction for secondary extinction was applied; its value was 9.2×10^{-7}. A final difference Fourier map showed several peaks less than 0.4 e/Å^3 scattered about the unit cell without a significant feature. The discrepancy indices R and R_w are presented with other pertinent data in Table I.

Results and Discussion

The atomic positional and thermal parameters are listed in Table II. Table III presents the important bond lengths and angles. Figure 1 is an ORTEP view showing the numbering scheme of the $[Cr(H_2O)_5(NO)]^{2+}$ ion. The packing diagrams of cations and SO_4 anions are presented as a stereoview in Figure 2. The structure consists of hydrogen-bonded dimers of $[Cr(H_2O)_5(NO)]$ (two O(4)–H···O(6) bonds, O(4)–O(6) = 2.832

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Table I. Crystallographic Data for $[Cr(H_2O)_5NO]SO_4$

formula	$CrH_{10}NO_{10}S$	ρ_{calcd}, g cm^{-3}	2.02
fw	268.14	T, °C	20
cryst syst	monoclinic	radiation (λ, Å)	Mo (0.710 69)
space group	$P2_1/n$	μ, cm^{-1}	15.27
a, Å	12.058(3)	unique reflcns	2541
b, Å	6.846(1)	reflcns with $I \geq 3\sigma(I)$	1854
c, Å	11.382(3)	refined params	129
β, deg	110.14(2)	R^a	0.033
V, Å^3	882.1(6)	$R_w{}^a$	0.045
Z	4	gof	1.45

[a] Function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$. $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Table II. Positional Parameters, B(eq) Values, and Estimated Standard Deviations for $[Cr(H_2O)_5(NO)]SO_4$

atom	x	y	z	B(eq), Å^2
Cr	0.48740(3)	0.25572(5)	0.21451(3)	1.41(1)
O(1)	0.5510(2)	0.2225(3)	0.3991(2)	2.42(7)
O(2)	0.3249(2)	0.1738(3)	0.2024(2)	2.56(7)
O(3)	0.4352(2)	0.5210(2)	0.2626(2)	1.78(6)
O(4)	0.4196(2)	0.3480(3)	0.0375(2)	2.67(8)
O(5)	0.6406(2)	0.3835(3)	0.2249(2)	2.52(7)
O(6)	0.5578(2)	−0.1255(3)	0.1628(2)	3.25(9)
N	0.5278(2)	0.0334(3)	0.1808(2)	1.99(8)
S	0.29357(5)	0.25104(9)	0.50964(5)	1.48(2)
O(7)	0.4199(2)	0.2948(3)	0.5394(2)	2.22(7)
O(8)	0.2800(2)	0.0383(2)	0.5234(2)	2.64(7)
O(9)	0.2279(2)	0.3013(3)	0.3768(2)	1.96(6)
O(10)	0.2459(2)	0.3561(3)	0.5931(2)	2.55(8)
H(1)	0.5083	0.2451	0.4428	2.3(7)
H(2)	0.6036	0.1294	0.4375	4.7(9)
H(3)	0.2889	0.2137	0.2539	2.3(6)
H(4)	0.2999	0.0483	0.1770	8(1)
H(5)	0.4882	0.5814	0.3306	3.5(7)
H(6)	0.3904	0.6042	0.2036	2.5(6)
H(7)	0.3622	0.4183	0.0180	4.3(9)
H(8)	0.4240	0.2909	−0.0306	8(1)
H(9)	0.6864	0.3310	0.1999	3.4(8)
H(10)	0.6797	0.4577	0.2766	6(1)

Table III. Selected Bond Distances (Å) and Angles (deg) for $Cr(H_2O)_5(NO)]SO_4$

	Distances		
Cr–O(1)	1.986(2)	Cr–O(5)	2.010(2)
Cr–O(2)	1.997(2)	Cr–N	1.682(2)
Cr–O(3)	2.057(2)	O(6)–N	1.186(3)
Cr–O(4)	1.999(2)		
	Angles		
O(1)–Cr–O(2)	93.06(9)	O(2)–Cr–N	94.9(1)
O(1)–Cr–O(3)	82.05(7)	O(3)–Cr–O(4)	86.15(8)
O(1)–Cr–O(4)	167.90(8)	O(3)–Cr–O(5)	87.68(8)
O(1)–Cr–O(5)	88.57(9)	O(3)–Cr–N	177.1(1)
O(1)–Cr–N	95.8(1)	O(4)–Cr–O(5)	88.28(9)
O(2)–Cr–O(3)	83.30(8)	O(4)–Cr–N	96.1(1)
O(2)–Cr–O(4)	88.20(9)	O(5)–Cr–N	94.3(1)
O(2)–Cr–O(5)	170.51(9)	Cr–N–O(6)	177.0(2)

Å, each) centered at the (1/2, 0, 0) and (0, 1/2, 1/2) inversion points of the unit cell. All the other hydrogen atoms are bonded to oxygen atoms of the $SO_4{}^{2-}$ ions (O–O = 2.623–2.814 Å). The severe distortion of bond angles of the cation (up to 12°) from ideal octahedral is most probably due to this extensive hydrogen-bonded packing.

The magnetic moment $\mu_{eff} = 2.02\,\mu_B$ indicates a single unpaired electron in $[Cr(H_2O)_5NO]^{2+}$. A similar low magnetic moment of 1.87 μ_B was reported[2] for $[Cr(CN)_5NO]^{3-}$, but the formulation $[Cr^{I}(NO)(CN)_5]^{3-}$, based on this evidence, had to be abandoned in favor of $[Cr^{III}(NO)(CN)_5]^{3-}$, on the basis of the chromium 3p electron-binding energy, which is almost identical to the value for known Cr(III) complexes.[16] Both complexes are $[M(NO)]^5$ in Feltham's notation.[20] The only valid conclusion from the low magnetic moments of the two complexes is that four out of five, originally unpaired, electrons that resided on the metal *and* the ligand, are spin-paired in these complexes (probably by π bonding).

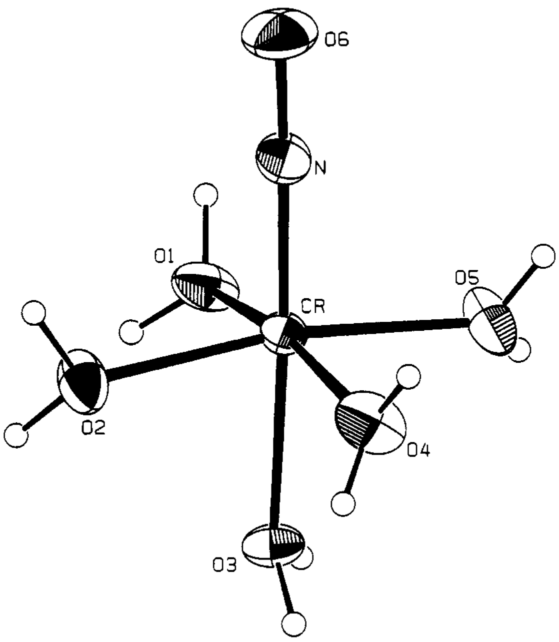

Figure 1. Structure of $[Cr(H_2O)_5(NO)]^{2+}$. Each atom (except H atoms) is represented by its ellipsoid of thermal displacement drawn at the 50% probability level.

The N–O stretching frequency ν = 1733 cm^{-1} is in the region 1600–1750 cm^{-1} which is indeterminate for discrimination between "NO^{+}" and "NO^{-}".[21] It is noteworthy that corresponding magnetic and infrared data of the "brown ring" compound $[Fe(H_2O)_5NO]^{2+}$ (μ = 3.80–3.97 μ_B; ν = 1765 cm^{-1}) led to the assignment of a high-spin Fe(I) to the iron atom and of NO^+ to the nitrosyl ligand.[2] This assignment had to be replaced later by Fe(III) and NO^-, because the Mössbauer spectrum was characteristic for a high-spin Fe(III) compound.[21]

It is now generally accepted that "the most reliable method for assignment of the coordination mode of nitric oxide in transition metal complexes in the solid state is single-crystal X-ray crystallography".[17]

The short Cr–N distance of 1.682(2) Å indicates multiple bonding between the chromium and nitrogen atoms. The bonding in most nitrosyl complexes is dominated by covalent interactions with the metal atom; therefore the assignment of precise oxidation numbers (integers) is not desirable.[20] At best, such assignments should be regarded as reasonable approximations. "NO^-" and "NO^+" are used to represent these approximations.[20] Bearing these limitations in mind, the following structural data support a residual charge on the chromium in $[Cr(H_2O)_5NO]^{2+}$ similar to that in complexes with a formal oxidation state +3 (and the corresponding oxidation number +1 for nitrogen, as in NO^-) rather than +1 for chromium (and +3 for nitrogen, as in NO^+):

(1) The average Cr–O_w distance of the four water ligands in the cis position to NO is 1.998 Å. This is characteristic for Cr–O_w in similar chromium(III) aqua complexes.[22] It is considerably shorter than Cr(II)–O_w distances, e.g. 2.106(2) Å in $[Cr(H_2O)_6]SiF_6$.[23] No Cr(I)–O_w distances are known, but if they exist they are expected to be longer than Cr(II)–O_w and certainly longer than Cr(III)–O_w distances.

(2) The Cr–O_w trans to NO is longer than the average cis Cr–O_w by 0.059 Å. Such a trans bond lengthening by a linear

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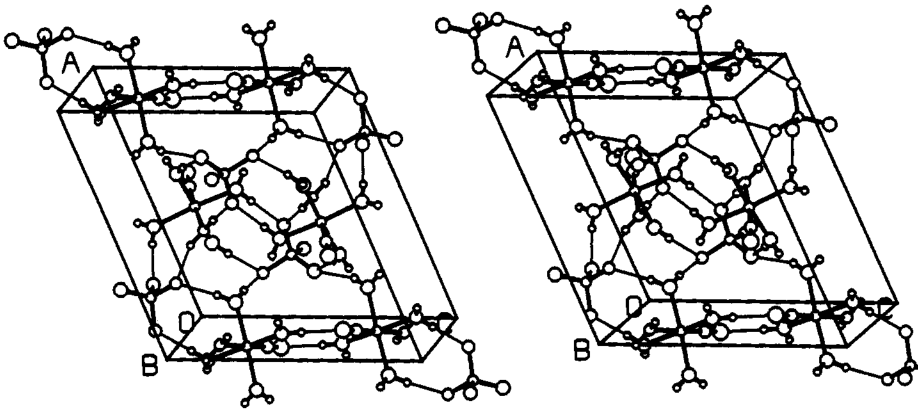

Figure 2. Packing diagrams of $[Cr(H_2O)_5(NO)]^{2+}$.

NO ligand indicates "NO^-", whereas trans bond shortening indicates "NO^+".[20]

The crystallographic data rule out the formulation $[Cr^INO(H_2O)_5]^{2+}$ and support an approximate oxidation number of +3 for the chromium atom. While the $[Cr^INO(H_2O)_5]^{2+}$ formulation is misleading and should be abandoned, it should not be substituted by the oversimplified, but essentially correct, formulation $[Cr^{III}(H_2O)_5NO]^{2+}$. One should refrain from using such explicit formulas for nitrosyl complexes of this type and be satisfied with the conventional $[Cr(H_2O)_5NO]^{2+}$ formulation. The analogy between this chromium complex and the "brown ring" complex, $[Fe(H_2O)_5NO]^{2+}$, is far reaching: Since the approximate residual charge on both metal atoms is +3, their nitrosyl ligands should be very similar if not identical. There is, indeed, a striking resemblance between the UV–vis spectra of the two complexes. Both have three absorption bands at similar wavelengths: The chromium complex[1] at 323, 449, and 559 nm and the iron complex[24a,b] at 335, 445, and 584 nm. These bands are probably associated with the common "NO^-" ligand.

Supplementary Material Available: Tables of U values and bond angles and distances (5 pages). Ordering information is given on any current masthead page.

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