

Characterization of the Geometric Isomers of the Tetraaquobispyridinechromium(III) Ion

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Tetraaquobispyridinechromium(III) ion

The geometric isomers of a number of $M(H_2O)_4X_2^{n+}$ ions, where M represents an octahedrally coordinated metal and X a ligand, have been characterized both on the basis of the usual observation that the *trans* isomer is easier eluted from a cation-exchange column than the *cis* isomer and using the rule that the *trans* isomer shows lower absorption intensity in the d-d transition bands region than the *cis* isomer. Recently, deviation from these simple rules for tetraaquobis-(pyridine N-oxide)chromium(III) ions was inferred from equilibria studies and the bulkiness of the ligand was tentatively suggested as the likely reason¹. We report here, using data on kinetics of the aquation, that the two rules are obeyed by the geometric isomers of the analogous disubstituted chromium(III) ion with similarly bulky pyridine ligand.

A long known but geometrically not characterized tetraaquobispyridinechromium(III) perchlorate² was eluted from a Dowex 50W-X8 cation-exchange column with 3M HClO₄. The successive eluents showed a constancy of UV-visible spectra throughout, the behavior compatible with isolation of a pure isomer (isomer I) having absorption (molar absorption coefficient follows in parenthesis) at: 533 nm, max. (25.9), 458 nm, min. (8.15), 393 nm, max. (35.6), 347 nm, min. (9.50), 259 nm, max. ($6.87 \cdot 10^3$), 238 nm, min. ($2.15 \cdot 10^3$), 213 nm, max. ($2.05 \cdot 10^4$), 208 nm, min. ($2.00 \cdot 10^4$).

The other isomer (isomer II) was prepared by the stepwise aquation of a triaquotripyridinechromium(III) species and by the subsequent separation on cation-exchange column. The latter species, which was obtained in solution by the reaction of mercury(II) perchlorate with trichlorotripyridinechromium(III), loses the first pyridine with $k = 3.62 \cdot 10^{-4} \text{ s}^{-1}$ and the second pyridine with $k = 9.45 \cdot$

10^{-5} s^{-1} at 85 °C in 1.0 M HClO₄, as revealed by the spectrophotometric investigation of the rate of aquation at the isosbestic point of pyridine and pentaquopyridinechromium(III) ion at 232.5 nm. The successive eluents from a Dowex 50W-X8 ion-exchange column containing previously separated bispyridine intermediate species showed constancy of the UV-visible spectra with absorption at: 536 nm, max. (23.4), 454 nm, min. (6.03), 392 nm, max. (24.6), 351 nm, min. (7.77), 260 nm, max. ($6.13 \cdot 10^3$), 237 nm, min. ($1.32 \cdot 10^3$), 215 nm, sh. ($9.24 \cdot 10^3$).

The higher absorption in the visible region of the isomer I, with the area under the first two d-d transition bands being 31% greater than that of the isomer II, indicates to *cis* configuration of isomer I and to *trans* configuration of isomer II³. Conformable with this indication is the behavior of the isomers on an ion-exchange column. After being loaded on the column in an equal amount and on elution with 1.5 M HClO₄, the amounts of the isomers in the eluents were determined using the high difference in molar absorption coefficient at 215 nm. Although no complete separation was achieved, their relative amounts in the successive eluents systematically changed from the pure *trans* (isomer II) at the beginning to the almost pure *cis* (isomer I) at the end of elution.

The determination of the geometric configuration of the isomers of tetraaquobispyridinechromium(III) ion is supported by the kinetics of the aquation. The substitution of the first pyridine in the *trans* and *cis* isomer proceeds with $k = 1.78 \cdot 10^{-4} \text{ s}^{-1}$ and $k = 5.88 \cdot 10^{-4} \text{ s}^{-1}$ at 90 °C in 1.0 M HClO₄, while pentaquopyridine species was found to aquate with $k = 5.86 \cdot 10^{-5} \text{ s}^{-1}$ under the same condition⁴. No substantial rate acceleration by the *trans* pyridine ligand is to be expected and the ratio 3.0 found between the aquation rates of the *trans*-bispyridine and the monopyridine complexes is not too far from the statistical factor of 2. The higher aquation rate of the *cis*-bispyridine complex is compatible with an expected steric interference between the *cis* pyridine ligands.

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