

Geometry of a Ligand-field Excited State of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$

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Summary Irradiation of metal ion absorption bands of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ produces *trans*- $\text{Rh}(\text{NH}_3)_4\text{OH}_2\text{I}^{2+}$ with 90% efficiency, suggestive of a square-pyramidal geometry for the ligand-field excited state.

It has frequently been suggested¹ that the thermally equilibrated excited states of co-ordination complexes differ in geometry from their ground states. The evidence, both photochemical and spectroscopic, supporting such speculation has thus far been indirect and equivocal. We have now obtained strong photochemical evidence that some of the ligand-field excited states of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ are indeed very greatly distorted.

The metal ion centred absorption bands of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ are very broad² and apparently correspond to ${}^1E \leftarrow {}^1A_1$ and ${}^1A_2 \leftarrow {}^1A_1$ transitions³ (λ_{max} 415 and 388 nm, respectively). A single rhodium complex, $\text{Rh}(\text{NH}_3)_4\text{OH}_2\text{I}^{2+}$, results from the irradiation of either of these *d-d* absorption bands. The product yield is high (0.85 ± 0.08) and independent of irradiating wavelength through this spectral region. The product, *trans*- $\text{Rh}(\text{NH}_3)_4\text{OH}_2\text{I}^{2+}$, has been

characterized spectroscopically. It has also been converted into the *trans*- $\text{Rh}(\text{NH}_3)_4\text{I}_2^+$ complex, which can easily be separated from the photolyte by chromatography, recrystallized, and analysed for elemental composition, as well as compared spectroscopically with the better known *trans*- $\text{Rh}(\text{en})_2\text{I}_2^+$.⁴ We have been unable to detect any *cis*-complexes among the reaction products.

When $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ was irradiated at 420 nm in 0.01M-NaI, we found the quantum yield for I^- exchange to be only 4% of that for formation of *trans*- $\text{Rh}(\text{NH}_3)_4\text{OH}_2\text{I}^{2+}$.

These results clearly imply that irradiations of the ligand-field absorption bands of $\text{Rh}(\text{NH}_3)_5\text{I}^{2+}$ result in the formation of an excited-state species in which the $\text{Rh}-\text{NH}_3$ bond *trans* to I^- is greatly weakened or broken. Thus the implicated excited state species must be nearly square pyramidal with an apical I^- . Although large excited-state distortions are consistent with the broad absorption bands, it is not yet known whether the photochemically active state is a singlet or triplet excited state. Whatever the spin multiplicity the excited state has a formal ($t_{2g}^5 e_g$) electronic configuration in which population of the antibonding e_g

orbitals is consistent with appreciable lengthening of some metal-ligand bond or bonds.

It has been observed that the ligand-field absorption bands of the analogous cobalt(III) complexes are photochemically insensitive (quantum yields generally less than 10^{-3}),^{1c} suggesting that the magnitude of the ligand-field stabilization energy is significant in determining the distortions produced in excited-state species. However, such a view is of limited value in a detailed accounting for the properties of the excited-state species since I^- appears to be tightly bound in the rhodium(III) excited states while Cl^- is not; *i.e.*, the only product of ligand-field irradiation

of $Rh(NH_3)_5Cl^{2+}$ is $Rh(NH_3)_5OH_2^{3+}$.⁵ Our work has shown that the bromopentammine complex exhibits intermediate behaviour, with both $Rh(NH_3)_5OH_2^{3+}$ and *trans*- $Rh(NH_3)_4OH_2Br^{2+}$ occurring as significant photochemical products. These observations are consistent with similar gross geometries for the excited states of the various halogenopentammines of rhodium(III), but the differences in bond lability suggest some differences in the nature of the metal-ligand bond between excited state and ground state species.

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¹ For example see: (a) A. W. Adamson, *J. Phys. Chem.*, 1967, **71**, 798; (b) H. L. Schläfer, *ibid.*, 1965, **69**, 2201; (c) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, 1970.

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⁵ L. Moggi, *Gazzetta*, 1967, **97**, 1089.