Molecular Nitrogen as a Ligand: the Crystal Structure of Nitrogenpentammineruthenium(II) Dichloride

By F. BOTTOMLEY and S. C. NYBURG

(*Lash Miller Chemical Laboratories, University of Toronto, Toronto 5, Canada*)

THE discovery of the complexes $[Ru^{II}(NH_3)_5N_2]X_2$, where $X{=}Br^-$, I^-, BF_4^-, PF_6^-, was recently reported from these laboratories by Allen and Senoff.[1] More recently we have prepared crystals of the previously unknown dichloride and dithionate salts.

A detailed *X*-ray structural examination has been made of the dichloride, a less detailed study of the di-iodide, and only preliminary examinations of other salts (except PF_6^-). With the possible exception of the dithionate these salts appear isomorphous, crystallizing in the cubic system, $Z = 4$ molecules per cell, space group either $Fm3m$, $F\bar{4}3m$, or $F432$. The *a* cell dimensions in Å are: Cl^-, 10·19; Br^-, 10·41; I^-, 10·94; BF_4^-, 11·166; $S_2O_6^{2-}$, 11·23 (?). The unit cell data and space group for BF_4^- agree with those found by Ibers.[2]

We initially undertook an X-ray study of the di-iodide, being unable at that time to obtain suitable crystals of the complex with other anions. With 100 independent reflections, measured photographically, we were able to locate only the six nitrogen atoms lying closest to the ruthenium, but could not be certain of the location of the remaining nitrogen atom except that it must, by symmetry, be statistically disordered. Data for the dichloride were collected using a diffractometer with Mo-K_α radiation. The intensities of 235 reflections were measured and averaged, to give 108 independent reflections, of which three (in the range of sin θ from 0 to 0·5) were immeasurably small and not used in the refinement.

In the particular case of these crystal structures the three possible space groups, $Fm3m$, $F\bar{4}3m$, and $F432$, become equivalent, since all the atoms are in special positions. The structure, Figure 1, must be disordered, the N_2 moiety randomly occupying the six octahedral positions around the ruthenium. Hence it is not possible to distinguish between the 5 NH_3 groups and the nitrogen atom N(1) of N_2, which is bonded directly to the ruthenium.

Using this disordered model the structure has been refined by full matrix least-squares method (anisotropic thermal motion, nine variable parameters) to $R = 0{\cdot}05$. The distance between Ru and the outer nitrogen atom is estimated as Ru · · · N(2), 3·23 ± 0·05 Å. Unfortunately, because of the disorder, this distance cannot be accurately partitioned but the refinement yields Ru–N(1), 2·11 Å; N(1)–N(2), 1·12 Å.

The close agreement between observed and calculated X-ray intensities coupled with a clearly defined N(2) atom on a difference synthesis leads to the definite conclusion that the system Ru–N–N is linear and that the bonding is therefore analogous to that in the metal carbonyls.

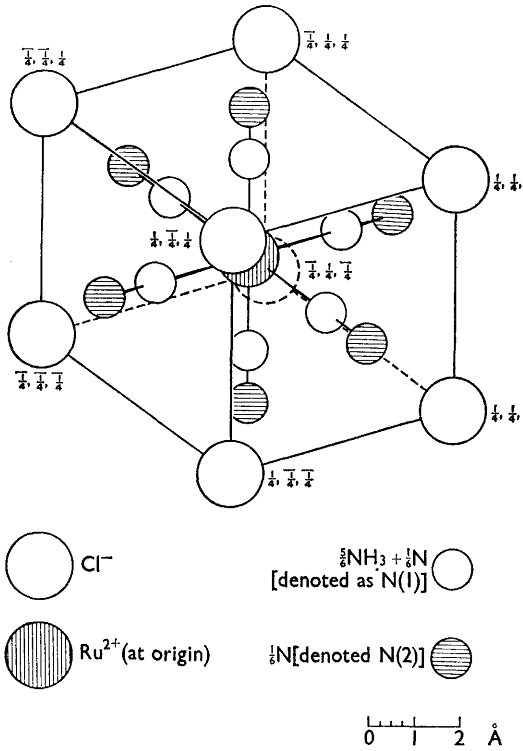

FIGURE 1

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[1] A. D. Allen and C. V. Senoff, *Chem. Comm.*, 1965, 621.

[2] D. J. Hodgson and J. A. Ibers, private communication.