

## Investigation of Pentamminenitrosyliron Dichloride by Mössbauer Spectroscopy

By H. MOSBÆK and K. G. POULSEN\*

(Chemistry Department A, The Technical University of Denmark, Lyngby, Denmark)

**Summary** Mössbauer spectroscopy has shown that  $[\text{Fe}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$  is an iron(III) compound.

In connection with the application of Mössbauer spectroscopy to problems of metal complex configurations, we have determined the Mössbauer parameters for  $[\text{Fe}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ .

This compound was formulated as an iron(I) compound by Griffith, Lewis, and Wilkinson.<sup>1</sup> They found an N-O stretching frequency at  $1754\text{ cm.}^{-1}$ , *i.e.* in a region considered<sup>2</sup> characteristic for co-ordinated  $\text{NO}^+$ . Unfortunately, it was not possible for the authors to verify the implied presence of  $\text{Fe}^I$  by their subsequent measurements of the magnetic susceptibility of the compound.

We made several preparations of the compound following the procedure of Weitz and Muller,<sup>3</sup> the method also used by Griffith *et al.* The freshly prepared compound is black,

but turns light brown (at a rate which makes the developing colour change just visible for the unaided eye) within approximately 1 hr. at room temperature.

The Mössbauer parameters were determined on the solid compound wafered between aluminium foils at approx.  $25^\circ$  with an Elron Mössbauer Effect Analyzer. Commercial sources of  $^{57}\text{Co}$  in stainless steel as well as in palladium were used. Countings spaced at  $0.02\text{ mm./sec.}$  allowed us to obtain the information required in 3–4 hr. After this lapse of time the sample still consisted predominantly of the black compound. The isomer shift relative to sodium nitroprusside was  $0.80 \pm 0.02\text{ mm./sec.}$  and the quadrupole splitting  $1.40 \pm 0.02\text{ mm./sec.}$ , respectively. The magnitude of the isomer shift is characteristic for high-spin iron(III) compounds.<sup>4</sup> After this surprising discovery, the i.r. spectrum of the compound was investigated (Perkin Elmer model 337 spectrophotometer, KBr disc). It was

found that absorption at approx.  $1750\text{ cm.}^{-1}$  was noticeable in the samples only after some aging ( $\sim 1\text{ hr.}$ ) accompanied by the colour change to brown. Freshly prepared samples showed absorption at approx.  $1600\text{ cm.}^{-1}$ , a frequency which has been assigned<sup>5</sup> to co-ordinated  $\text{NO}^-$ . In order to distinguish between  $\text{NO}$  co-ordinated as  $\text{NO}^-$  and  $\text{N}_2\text{O}_2$ :<sup>2-</sup> the compound was decomposed with sulphuric acid and the products were found to be  $\text{Fe}^{\text{II}}$  and  $\text{NO}$ , indicating that the compound is monomeric.<sup>6</sup> This was also confirmed on a sample which had been used for the Mössbauer study. We conclude that the black compound should be formulated as  $[\text{Fe}^{\text{III}}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ .

A closer examination of the Mössbauer parameters reveals that the isomer shift is somewhat larger than expected. This can be understood in terms of a  $\pi$ -bonding between the  $\pi^*$ -orbitals of  $\text{NO}$  and the  $d_{zy}$ ,  $d_{zx}$ -orbitals of iron. Such bonding is generally assumed in the case of  $\text{NO}^+$  co-ordination, where in most cases a considerable amount of

back-donation takes place in this way.<sup>7</sup> On account of the half-filled antibonding orbitals in  $\text{NO}^-$  it is reasonable to assume that some of the antibonding electrons are transferred to the  $d$ -orbitals of the iron atoms. This will lead to an increased number of  $d$ -electrons as compared, *e.g.*, with iron in a hexammine iron(III) complex, and thereby cause an increased screening of the  $s$ -electrons. In iron compounds this will result in an increased isomer shift.<sup>8</sup> The quadrupole splitting, which is larger than any previously measured on high-spin iron(III) compounds, can be explained in a similar way. The  $\pi$ -bonding will disturb the spherical symmetry of the exactly half-filled  $3d$ -shell of iron and thereby cause an electric field gradient.

Successful measurements of the magnetic susceptibility would add valuable new information to help in the understanding of this interesting compound.

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<sup>1</sup> W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Chem. Soc.*, 1958, 3993.

<sup>2</sup> J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, 7, 32.

<sup>3</sup> E. Weitz and H. Müller, *Angew. Chem.*, 1950, 62, 221.

<sup>4</sup> W. Kerler, N. Neuwirth, and E. Fluck, *Angew. Chem.*, 1963, 75, 461.

<sup>5</sup> E. E. Mercer, W. A. McAllister, and J. R. Durig, *Inorg. Chem.*, 1967, 6, 1816.

<sup>6</sup> W. Silverthorn and R. D. Feltham, *Inorg. Chem.*, 1967, 6, 1662.

<sup>7</sup> F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 1st edn., Interscience, New York, 1962, p. 627.

<sup>8</sup> L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters*, 1961, 6, 98.