

## Nuclear Quadrupole Resonance in Coordination Chemistry. Identification of Bridging and Terminal Chlorines in the Mercuric Chloride-4-Picoline *N*-Oxide Complex

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### Abstract

The temperature dependence of the chlorine-35 n.q.r. in the mercuric chloride-4-picoline *N*-oxide complex has been studied from 77 K to room temperature, and the results are used to assign the observed frequencies to terminal and bridging chlorines.

Mercury(II) halides form a number of complexes of the formula  $(\text{HgX}_2)_n\text{L}_m$  with oxygen donor ligands. Widely varying structures<sup>1</sup> have been postulated for these complexes based on various physicochemical techniques. Brill *et al.*<sup>2-4</sup> have studied a number of mercury(II) halide complexes by halogen n.q.r. spectroscopy. They have correlated the n.q.r. frequencies with the structures of these complexes and have concluded that those complexes which give a single resonance frequency have a four-coordinate structure as in  $\text{HgCl}_2$ -dioxan.<sup>5</sup> Complexes which show two well resolved (at least by about 1.0 MHz) resonances have been assigned a bridge structure with halogen bridges. Recently Wulfsberg<sup>6</sup> has pointed out the complexity of the interpretation of n.q.r. frequencies in mercury(II) halide complexes. The existing n.q.r. data have been analysed by Wulfsberg who showed that they could be used for predicting the coordination number of mercury(II) in these complexes.

A temperature-dependence study of the halogen n.q.r. frequencies may help in assigning the frequencies to terminal and bridging halogens in a dimeric structure with halogen bridges. Due to torsional oscillations, the electric-field gradients at both the bridging and terminal halogens will be averaged; as the temperature increases, the averaging becomes more pronounced, and hence a decrease in the n.q.r. frequency is observed. Since the amplitude of the torsional oscillations at the bridging site is expected to be smaller than that at the terminal halogen site, it may be presumed that the averaging of the electric-field gradient at the bridging halogen site would be smaller than that at the terminal site. This would result in a lower temperature coefficient  $(\partial\nu/\partial T)_p$  for the bridging halogen than for the terminal one. We have confirmed this by studying the temperature dependence of the chlorine-35 n.q.r. in the mercuric

<sup>1</sup> Grdenic, D., *Q. Rev., Chem. Soc.*, 1965, 19, 303.

<sup>2</sup> Brill, T. B., and Hugus, Z. Z., Jr, *J. Inorg. Nucl. Chem.*, 1971, 33, 371.

<sup>3</sup> Brill, T. B., *Inorg. Nucl. Chem.*, 1970, 32, 1869.

<sup>4</sup> Brill, T. B., Hugus, Z. Z., Jr, *Inorg. Chem.*, 1970, 9, 984.

<sup>5</sup> Hassel, O., and Hvorslef, J., *Acta Chem. Scand.*, 1954, 8, 1953.

<sup>6</sup> Wulfsberg, G., *Inorg. Chem.*, 1976, 15, 1791.

chloride-4-picoline *N*-oxide complex ( $\text{HgCl}_2\text{-mpyo}$ ). The results show that the bridging and the terminal chlorines can be clearly distinguished.

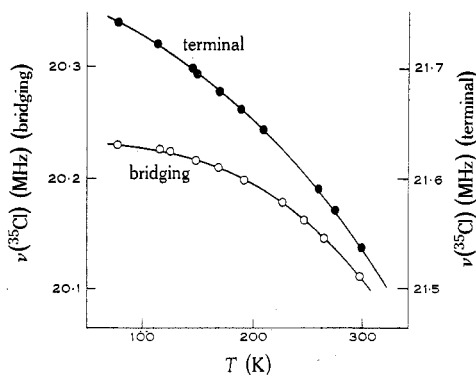


Fig. 1. Temperature dependence of the chlorine-35 n.q.r. in the  $\text{HgCl}_2\text{-mpyo}$  complex.

Two signals were reported at room temperature<sup>2</sup> for  $\text{HgCl}_2\text{-mpyo}$ . The compound also exhibits two  $^{35}\text{Cl}$  resonances at 77 K. The temperature-dependence data for the two  $^{35}\text{Cl}$  resonances are shown in Fig. 1. The low-frequency signal exhibits a lower temperature coefficient  $(\partial\nu/\partial T)_p$  compared with that of the high-frequency line. Further, the low values of  $(\partial\nu/\partial T)_p$  for both the resonances in  $\text{HgCl}_2\text{-mpyo}$  compared with  $(\partial\nu/\partial T)_p$  for  $\text{HgCl}_2$  indicate a damping of the torsional oscillations at the chlorine sites in  $\text{HgCl}_2\text{-mpyo}$  on complex formation.

Brill *et al.*<sup>2,4</sup> also have assigned the low-frequency signal to the bridging chlorine and the high-frequency one to the terminal chlorine. Our study of the temperature dependence of these resonance frequencies shows that this assignment is correct. The low-frequency line, which is assigned to the bridging chlorine, exhibits a lower  $(\partial\nu/\partial T)_p$  showing a smaller motional averaging of the electric-field gradient with temperature, consistent with the smaller amplitude at the site of the bridging chlorine. It can be seen from Fig. 1 that the two resonances exhibit a similar temperature dependence at higher temperatures (close to room temperature), while at lower temperatures the lower-frequency resonance becomes less and less temperature-sensitive. This shows that the dimer is held together rather weakly at the room temperature, with the bridging chlorine more or less as free as the terminal one. However, at lower temperatures, the bridging chlorine is much less free than the terminal one; this indicates that the dimeric structure stabilizes at lower temperatures (*c.* 200 K or less). Ultimately, the bridging chlorine becomes virtually unable to undergo torsional motions, as seen by n.q.r. around 125 K, while the terminal one continues to experience motional averaging of the electric-field gradient down to 77 K. This is indicated by the observation that the low-frequency resonance becomes almost independent of temperature below 125 K while the other resonance frequency continues to increase all the way down to 77 K.

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