Inorganica Chimica Acta, 14 (1975) L37 - L38
© Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Cis- and *Trans*-Isomers of $[Rh(en)_2X_2]^+$ where X = Cl and Br. Possible Use of ^{13}C NMR Spectroscopy in their Identification

C. BURGESS* and F. R. HARTLEY

Department of Chemistry, The University, Southampton SO9 5NH, U.K.

(Received June 4, 1975)

Although it has been shown that ^1H NMR spectroscopy can be used to distinguish the *cis*- and *trans*-isomers of $[Co(en)_2X_2]^+$,[1] the ^1H NMR spectra of the corresponding rhodium(III) complexes are virtually identical.[2] Following a recent report that the ^{13}C NMR spectra of *cis*-$[Co(en)_2X_2]^+$, where X = halide, showed two bands whereas those of the corresponding *trans*-complexes showed only one band[3] we recorded the ^{13}C NMR spectra of the analogous rhodium(III) complexes $[Rh(en)_2X_2]^+$, where X = Cl and Br. The results (see Table) indicate that whilst the *cis*-dichloro isomer does indeed show a more complex spectrum than the *trans*-isomer, both the dibromo complexes exhibit only a single ^{13}C NMR peak. Accordingly ^{13}C NMR cannot be used to distinguish *cis*- and *trans*-isomers of $[Rh(en)_2X_2]^+$, and distinction between these two isomers must therefore rest on infrared[4] and uv–visible[2] spectral investigation.

The observation of 3 bands, which were of approximately equal intensity, in the ^{13}C NMR spectrum of *cis*-$[Rh(en)_2Cl_2]^+$ is perhaps unexpected. However examination of all the possible ring conformations shows, assuming that conformational interconversions are slow on the NMR time scale, that there are 8 different carbon atom environments possible in *cis*-$[Rh(en)_2X_2]^+$ and 2 in the *trans*-isomer. Clearly the observation of 1 and 3 peaks respectively in *trans*- and *cis*-$[Rh(en)_2Cl_2]^+$ indicates that either not all the interconversions are slow or a number of accidental coincidences occur. Clearly in view of this the observation of only a single line in the spectrum of *cis*-$[Rh(en)_2Br_2]^+$ is not entirely unexpected.

In the course of this work it was necessary to prepare *cis*-$[Rh(en)_2Br_2]^+$. It has previously been reported that this can be prepared by refluxing the corresponding dichloro-complex with excess sodium bromide.[4] In following this method the refluxing was allowed to continue for about 75 minutes before cooling in ice. The uv–visible spectrum of this solution showed bands at 27,620 and 23,920 cm^{-1}, the former being that expected for the *cis*-dibromo product and the latter, which was only a weak shoulder, could have been due to the *trans*-dibromo isomer. When boiling was continued the band tentatively assigned to the *trans*-isomer grew in intensity and shifted to 23,360 cm^{-1} (in agreement with the literature value for *trans*-$[Rh(en)_2Br_2]^+$) whilst the band at 27,620 cm^{-1} diminished to a weak shoulder. No further change in the spectrum occurred when boiling was continued beyond 2¼ hours.

TABLE. ^{13}C NMR Chemical Shifts of $[Rh(en)_2X_2]^+Y^-$ Complexes.[a]

X	Y	Isomer[b]	Chemical shifts (ppm)[c]
Cl	Cl	*cis*[d]	46.3, 45.3, 44.9
Cl	NO_3	*trans*[e]	44.8[f]
Br	Cl	*cis*[d]	46.0
Br	NO_3	*trans*[e]	45.2

[a] Recorded on a Varian XL-100 spectrometer operating in the Fourier Transform mode at a frequency of 25.2 MHz with proton-noise decoupling.
[b] In view of the possibility of *cis* → *trans*-isomerisation the uv–visible spectra of all the solutions were recorded before and after the ^{13}C NMR spectra. No changes were observed and all the spectra agreed with those reported in the literature.[2]
[c] Chemical shifts, which are to low field of TMS, were determined in D_2O using 1,4-dioxane as an internal reference (assumed to lie 66.5 ppm to low field of TMS[7]) at a temperature of +33 °C unless otherwise stated.
[d] Prepared from *cis*-$[Rh(en)_2X_2]ClO_4$[2] by treatment with $^nBu_4NCl$ followed by filtration to remove the precipitated $^nBu_4NClO_4$.
[e] Prepared according to reference 4. [f] Recorded at +80 °C.

Since no thermal *cis* → *trans*-isomerisation of $[Rh(en)_2X_2]^+$ complexes in water has previously been reported except for X = I,[4] although thermal *cis* → *trans*-isomerisation in methanol has been reported for X = Cl and Br[5] and photochemical *cis* → *trans*-isomerisation in water is known for X = Cl,[6] we investigated whether or not the presence of excess bromide was necessary. When an aqueous

---

*Present address: Analytical Department, Glaxo Laboratories Ltd., Barnard Castle, County Durham, DL12 8DT, U.K.

solution of *cis*-[Rh(en)$_2$Br$_2$]ClO$_4$ was boiled there was a rapid change in the uv–visible spectrum that was largely complete within 15 minutes in which the band initially at 27,250 cm^{-1} was shifted to 28,170 cm^{-1} and a very weak shoulder at about 23,500 cm^{-1} appeared. This was consistent with the establishment of equilibrium (1), together with the formation of a trace of the *trans*-isomer:

$$cis\text{-}[Rh(en)_2Br_2]^+ + H_2O \rightleftarrows cis\text{-}[Rh(en)_2Br(H_2O)]^{2+} + Br^- \qquad (1)$$

On further boiling the lower energy shoulder slowly increased in intensity to a peak at 23,470 cm^{-1} at the expense of the high energy peak which, after 450 hours, was only a weak shoulder. A peak at 23,470 cm^{-1} is expected[2] for a solution containing *trans*-[Rh(en)$_2$Br$_2$]$^+$ together with a little *trans*-[Rh(en)$_2$Br(H$_2$O)]$^{2+}$. The slow step of this *cis* → *trans*-isomerisation does not appear to involve reaction of free bromide ion with either *cis*-[Rh(en)$_2$Br(H$_2$O)]$^{2+}$ or the 5-coordinate species [Rh(en)$_2$Br]$^{2+}$ since the reaction was not noticeably accelerated when performed in the presence of a 120-fold excess of sodium bromide. This is consistent with a dissociative mechanism.

We are currently investigating further the details of this previously unobserved isomerisation.

Acknowledgements

We thank Mrs. J. M. Street for recording the ^{13}C NMR spectra and the S.R.C. for a postdoctoral research assistantship (to C.B.) together with a grant towards the purchase of the Unicam SP 1700a spectrophotometer.

References

1 D. A. Buckingham, L. Durham and A. M. Sargeson, *Aust. J. Chem., 20,* 257 (1967).
2 C. Burgess, F. R. Hartley and D. E. Rogers, *Inorg. Chim. Acta, 13,* 35 (1975).
3 D. A. House and J. W. Blunt, *Inorg. Nucl. Chem. Lett., 11,* 219 (1975).
4 S. A. Johnson and F. Basolo, *Inorg. Chem., 1,* 925 (1962).
5 L. P. Gendernalik, *Ph.D. Thesis,* University of Detroit, 1970; *Diss. Abs., 31B,* 5860 (1971).
6 M. M. Muir and W.-L. Huang, *Inorg. Chem., 12,* 1831 (1973).
7 A. J. Jones, E. L. Eliel, D. M. Grant, M. C. Knoeber and W. F. Bailey, *J. Am. Chem. Soc., 93,* 4772 (1971).