

**A NEW SYNTHETIC ROUTE TO MIXED-METAL CLUSTERS $\text{Fe}_2\text{Ru}(\text{CO})_{12}$
 AND $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$
 A CRYSTAL STRUCTURE STUDY OF $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$**

TAPANI VENÄLÄINEN and TAPANI A. PAKKANEN

Department of Chemistry, University of Joensuu, P.O. Box 111, SF-80101 Joensuu 10 (Finland)

(Received May 29th, 1986)

Summary

The reaction of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ and $[\text{Fe}(\text{CO})_4]^{2-}$ in water solution gives the mixed-metal clusters $\text{Fe}_2\text{Ru}(\text{CO})_{12}$, $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ and variable amounts of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$. The reaction provides a practical route to $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$.

Structural and spectroscopic studies reveals that $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ crystallises together with $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ in the space group $C2/c$, the average structure closely resembling that of pure $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$. The ^1H NMR spectrum shows the fluxionality of $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ and provides a convenient method of analysis of the cluster mixture.

Introduction

Parent mixed-metal clusters of iron and ruthenium have been synthesized for catalytic investigations [1–5], for ligand substitution studies [6], and for starting materials for clusters of higher nuclearity [7–9]. The trinuclear iron–ruthenium mixed-metal clusters $\text{FeRu}_2(\text{CO})_{12}$, $\text{Fe}_2\text{Ru}(\text{CO})_{12}$ and $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ were made previously with variable yields by the reaction of $\text{Fe}(\text{CO})_5$ with either $\text{Ru}_3(\text{CO})_{12}$ or $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ [10]. $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ has been well characterized, but little is known of the other $\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ - and $\text{Fe}_3\text{Ru}(\text{CO})_{13}$ -core clusters. The neutral tetranuclear cluster $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ can be obtained along with $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ but it is difficult to separate the two species from each other. $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ has been detected by mass spectrometry in this mixture. The infrared spectrum of $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ was derived by monitoring the changes in the absorptions of the mixtures of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ and $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ in the chromatographed fractions [9].

The structure of the cluster $\text{HFe}_2\text{Ru}_2(\text{CO})_{13}^-$ is known and has in solid state one bridged carbonyl, differing from the structure of $\text{HFeRu}_3(\text{CO})_{13}^-$, which has in addition one semibridged carbonyl [11]. The structure of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ in

solution [12] and in solid state (space group $P2_1/a$) [13] is well known, but there are no reports of the structure of $H_2Fe_2Ru_2(CO)_{13}$.

We describe here a new synthetic route for $Fe_2Ru(CO)_{12}$ and $H_2Fe_2Ru_2(CO)_{13}$. Identification of $H_2Fe_2Ru_2(CO)_{13}$ reveals that $H_2Fe_2Ru_2(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$ crystallise as a mixture in the space group $C2/c$. The geometry of the disordered structure is similar to that of pure $H_2FeRu_3(CO)_{13}$.

Reagents

$[Ru(CO)_3Cl_2]_2$ was purchased from Strem Chemicals, and $[Fe(CO)_4]_2$ was prepared by a published procedure [14]. Water, n-hexane, and aqueous H_3PO_4 were deoxygenated by bubbling N_2 through them before use. All manipulations after acidification were conducted in air.

Synthesis

A solution of $[Fe(CO)_4]_2$ (1 g, 3.3 mmol) in 20 ml of water was added to a stirred suspension of $[Ru(CO)_3Cl_2]_2$ (0.51 g, 1 mmol) in 10 ml of H_2O . The brown solution was subsequently filtered and acidified with 40% H_3PO_4 in the presence of n-hexane. The hexane layer was separated, dried with $MgSO_4$, concentrated and chromatographed on a silica gel column. The fractions were in order: unidentified (yellow), green $Fe_3(CO)_{12}$, purple $Fe_2Ru(CO)_{12}$ (20%) and a final brown band containing $H_2Fe_2Ru_2(CO)_{13}$ (20%) and trace of $H_2FeRu_3(CO)_{13}$. The IR spectrum of $H_2Fe_2Ru_2(CO)_{13}$ in hexane (2105w, 2084s, 2073m, 2057s, 2042vs, 2023m, 2005vw, 1993vw, 1880w, 1860m cm^{-1}) shows no strong absorption at 2015 cm^{-1} , as reported earlier for this compound [9].

If the work-up procedure is varied the product distribution changes. When the synthesis was conducted with a 1/1 Fe/Ru mol ratio, the $H_2FeRu_3(CO)_{13}$ content in the tetranuclear mixture was about 40%. Increase in the amount of $[Fe(CO)_4]_2$ caused an increase in the yield of $Fe_3(CO)_{12}$ and a decrease in the amount of $H_2FeRu_3(CO)_{13}$ to 3%, the $H_2Fe_2Ru_2(CO)_{13}$ yield remaining unchanged.

The material used for the unit cell measurements and for the X-ray fluorescence study were obtained from a preparation in which a 1/1 metal ratio was used. The crystals were grown from a n-hexane solution.

The method described here for the synthesis of $Fe_2Ru(CO)_{12}$ is faster and simpler and gives better yields than those previously described.

Spectroscopy and X-ray diffraction

The infrared spectrum was recorded in n-hexane on a Perkin–Elmer 297 spectrophotometer using 0.5 mm NaCl solution cells.

The 1H NMR spectra were recorded on a Bruker AM-250 spectrometer with $CDCl_3$ as solvent. The chemical shifts are relative to TMS.

X-ray fluorescence spectra were obtained with an energy dispersive Electron Microprobe Analyser. A single crystal of pure $H_2FeRu_3(CO)_{13}$ was used to calibrate the metal ratio.

The data for the cell parameters were collected on a Nicolet R3M diffractometer. The refinement of the structure was carried out by the SHELXTL program package [15].

Results and discussion

The unit cell dimensions were measured for the brown tetranuclear compound. The dimensions (a 31.414, b 9.723, c 13.835 Å) were within the standard deviations the same as those of the material described as a second form of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ (II) [16]. X-ray fluorescence measurements indicated, however, that in our crystal iron formed 35 mol% of the metal content. Careful examination of the thermal parameters of compound II reveals an unusually large isotropic thermal parameter (3.45) for Ru(3) compared with the corresponding parameters for the two other ruthenium atoms (2.76, 2.46). These observations prompted us to recalculate the structure with the published structure factors of II.

When the published positional parameters and structure factors were used the refinement gave the same value for R (0.043) as reported before. Four calculations were then carried out by allowing the occupancy of each metal site to refine separately with variable Fe/Ru occupancy ratio. Only one of these refinements lead to a lowering of R (0.0313). The ruthenium occupancy of the metal labelled Ru(3) fell from unity to 0.633, indicating that 37% Fe is located at this site. This iron distribution corresponds to 34 mol% of the total metal content, in a good agreement with the X-ray fluorescence analysis.

The presence of iron at site Ru(3) has also an effect on the bond lengths of the published structure. The deviations of the metal–metal and metal–ligand distances in different ruthenium centers can be also understood in terms of the disorder in the Ru(3) center.

The ^1H NMR spectra of $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ at room temperature and at -50°C are shown in Fig. 1 and 2. Figure 1 shows a broad average signal for $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ and a sharp signal for $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$, with chemical shifts -20.27 and -18.6 ppm, respectively [12]. As the temperature is lowered, the coalesced resonances of $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ begin to broaden and then to sharpen to two signals at δ -18.5 and -21.7 ppm (Fig. 2). The signals were too broad for the measurement of the ^1H – ^1H coupling.

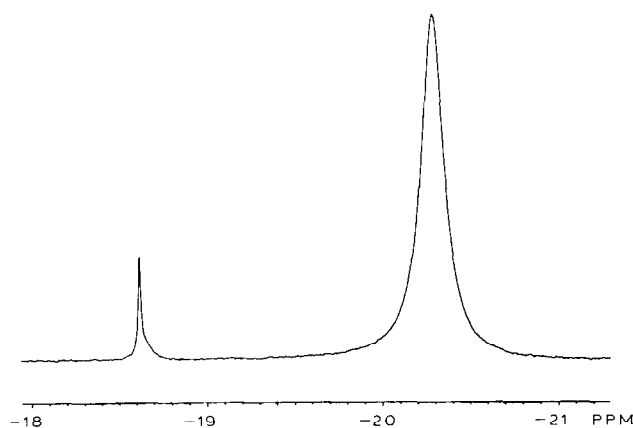


Fig. 1. ^1H NMR spectrum of $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ at room temperature. The resonance at -18.6 ppm is due to $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ impurity.

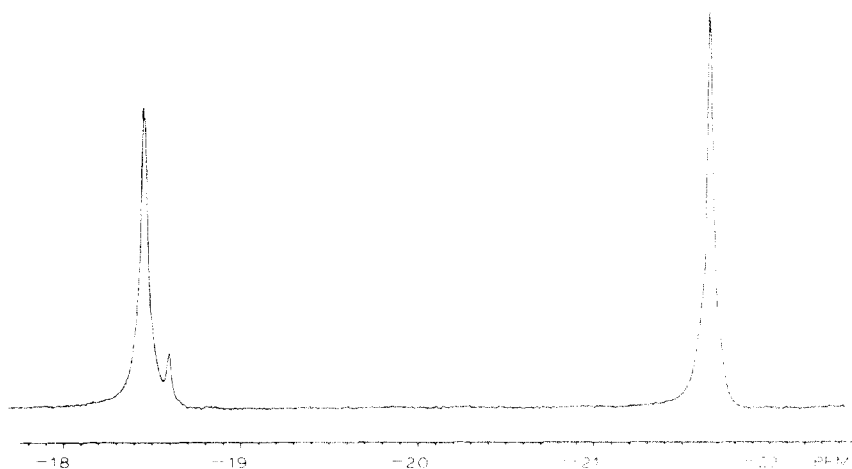


Fig. 2. ^1H NMR spectrum of $\text{H}_2\text{Fe}_5\text{Ru}_2(\text{CO})_{13}$ at -50°C .

All our infrared, ^1H NMR, and X-ray fluorescence data were in good agreement with the structure as recalculated. $\text{H}_2\text{Fe}_2\text{Ru}_2(\text{CO})_{13}$ appears to be the first example of a mixed-metal cluster of the iron group with a bond between iron and hydrogen.

References

- 1 T. Venäläinen, E. Iiskola, J. Pursiainen, T.A. Pakkanen and T.T. Pakkanen, *J. Mol. Catal.*, **34** (1986) 269.
- 2 P.C. Ford, *Acc. Chem. Res.*, **14** (1981) 31.
- 3 H.E. Ferkul, J.M. Berlie, D.J. Stanton, J.D. McCovan and M.C. Baird, *Can. J. Chem.*, **61** (1983) 1306.
- 4 L. Guzi, Z. Schay, K. Lazar, A. Vizi and L. Marko, *Surf. Sci.*, **106** (1981) 516.
- 5 Z. Schay and L. Guzi, *Acta Chim. Acad. Sci. Hung.*, **111** (1982) 607.
- 6 T. Venäläinen and T.A. Pakkanen, *J. Organomet. Chem.*, **266** (1984) 269.
- 7 P.C. Steinhard, W.L. Gladfelter, A.D. Harley, J.R. Fox and G.L. Geoffroy, *Inorg. Chem.*, **19** (1980) 332.
- 8 F.R. Furya and W.L. Gladfelter, *J. Chem. Soc. Chem. Commun.*, (1986) 129.
- 9 G.L. Geoffroy, and W.L. Gladfelter, *J. Am. Chem. Soc.*, **99** (1977) 7565.
- 10 D.B.W. Yawney and F.G.A. Stone, *J. Chem. Soc. A*, (1969) 502.
- 11 E. Takusava, A. Fumagalli, T.F. Koetzle, G.R. Steinmetz, R.P. Rosen, W.L. Gladfelter, G.L. Geoffroy, M.A. Bruck and R. Bau, *Inorg. Chem.*, **20** (1981) 3823.
- 12 W.L. Gladfelter and G.L. Geoffroy, *Inorg. Chem.*, **19** (1980) 2579.
- 13 C.J. Gilmore and P. Woodward, *J. Chem. Soc. A*, (1971) 3453.
- 14 R.G. Komoto, Dissertation in University of Stanford, 1974.
- 15 G.M. Shelrick, *The SHELXTE System*, Rev. 5, Nicolet Co., 1980.
- 16 L.-Y. Hsu, A.A. Bhattacharyya and S.G. Shore, *Acta Cryst., C*, **40** (1984) 722.