EPR spectra recorded at X-band (9.56 GHz) on the powder sample of **5'** show a temperature dependent change of the spectral shape. At room temperature only a single line with g = 2.1 is observed. On lowering temperature the g value remains constant down to 80K and only the intensity of the line increases. Below 80K, the rhombic pattern due to three principle g values becomes clearly visible in the spectra. The anisotropy of the g values increases with decreasing temperature and the average *g* factor slightly increases up to 2.12 at the lowest temperature.

As L. Banci et al.[1] and J. V. Slageren et al.[2] have discussed, such temperature dependence of the spectral shape of a trimer Cu^{II} complex can be related to a temperature driven change of the relative population of the spin states of the molecule (|1/2;1>, |1/2;0>, and |3/2;1>) and to a change of the interconversion rate between the spin states.

A characteristic modification of the spectral shape below 80K corresponds well with the temperature at which the slope of the inverse susceptibility $\chi(T)^{-1}$ changes (see Fig. 6); in both cases it can be related with the energy scale of the intratrimer exchange $J_{12} = J_{13} = -65\ cm^{-1} = 93.6$ K obtained from the fit of the $\chi(T)$ data.

1. L. Banci, A. Bencini, D. Gatteschi, *Inorg. Chem.,* 1983, **22**, 2681.
2. J. Van Slageren, A. Ahmedova, A. Gatteschi, C. A. Massa, L. A. Pardi, *Inorg. Chim. Acta*., 2003, **351**, 59.

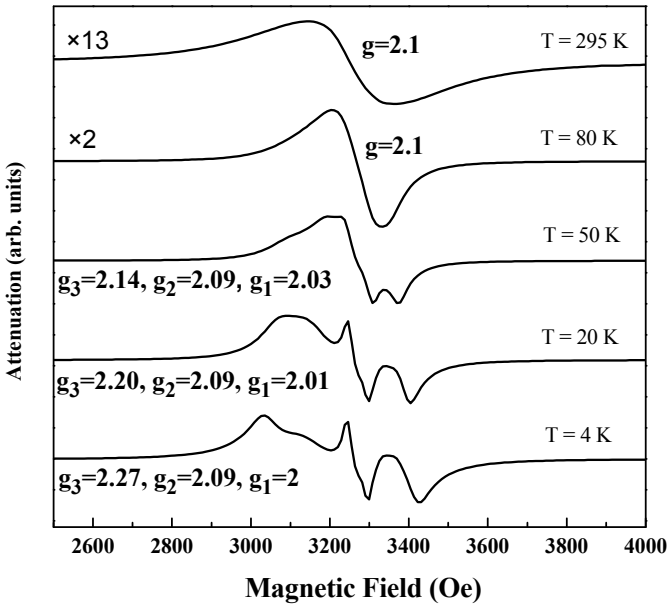

Fig.S1. Variable temperature X-band EPR spectra of **5'**. The *g* values are estimated from the modelling of the respective spectra that takes into account also the HF interaction with $^{63,65}Cu$ nuclei.

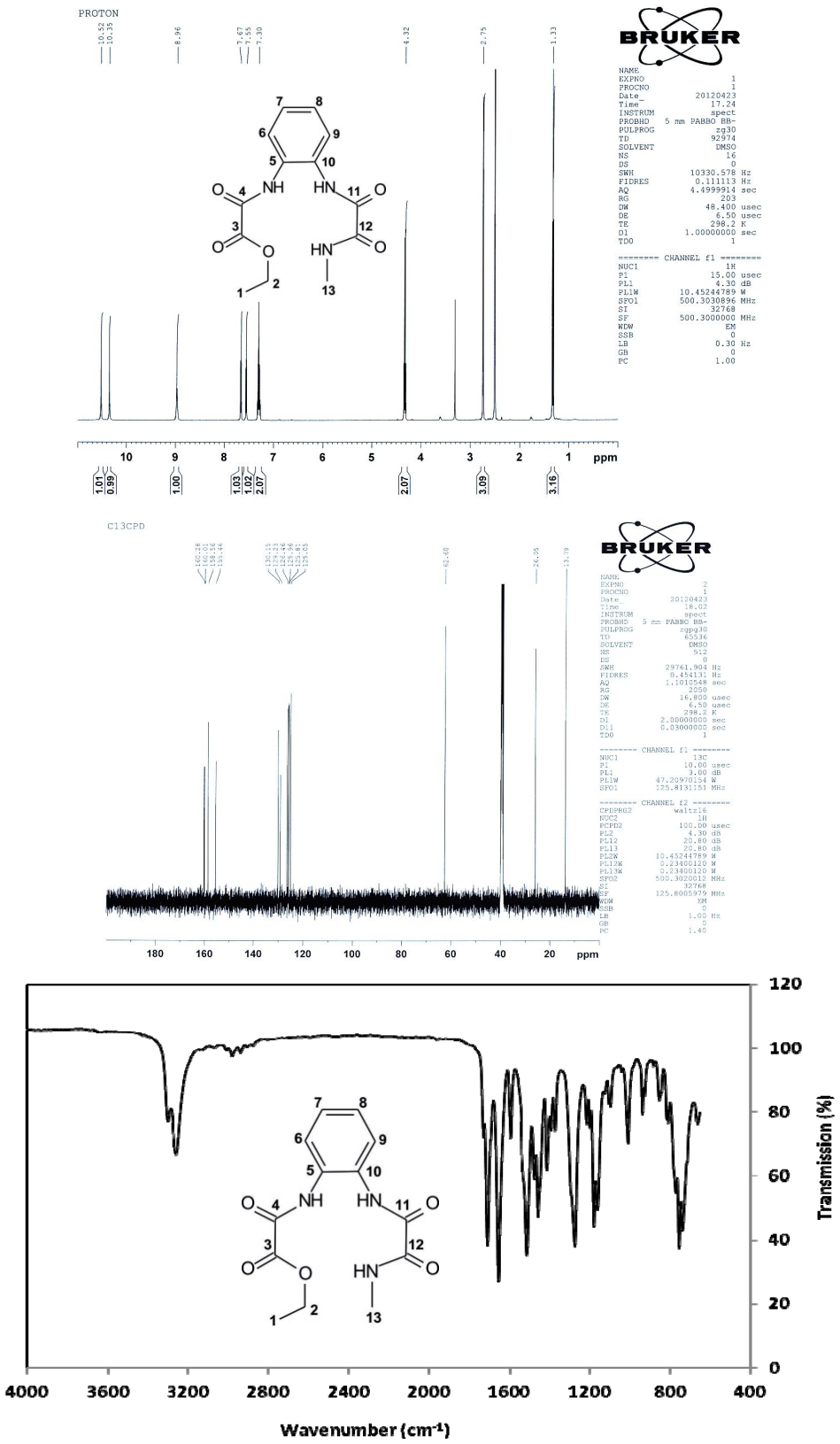

Fig. S2. ^{1}H (above), ^{13}C NMR (middle) and IR spectra (down) of **2**.

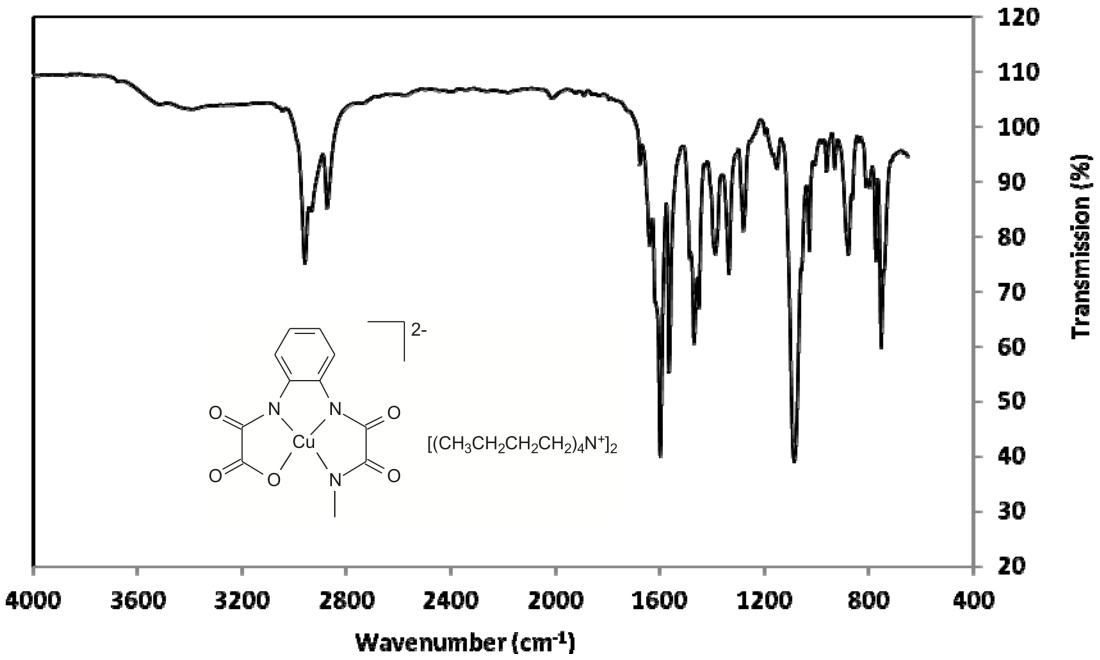

Fig. S3. IR spectrum of **3B**.

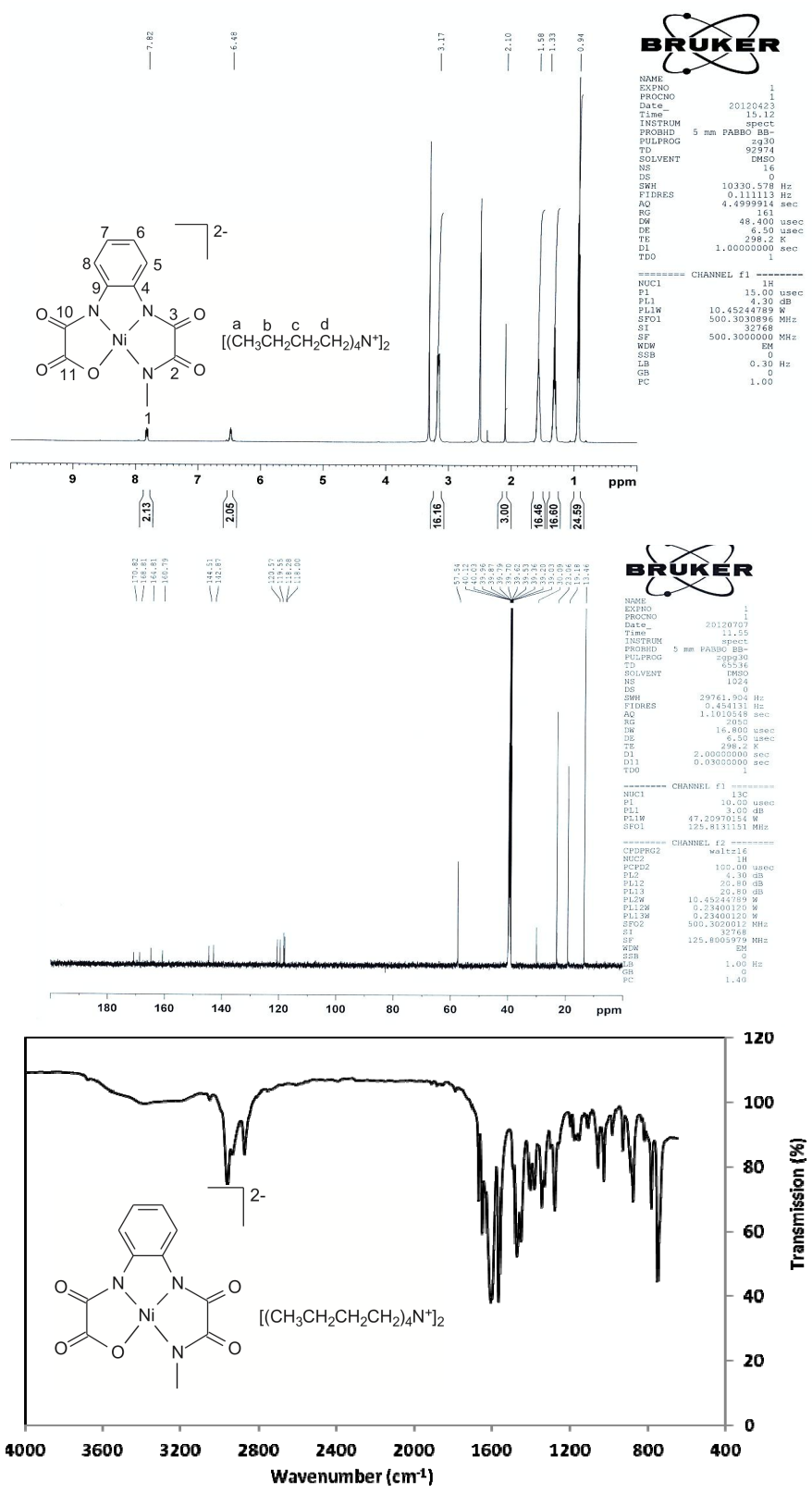

Fig. S4. ^{1}H (above), ^{13}C NMR (middle) and IR spectra (down) of **4**.

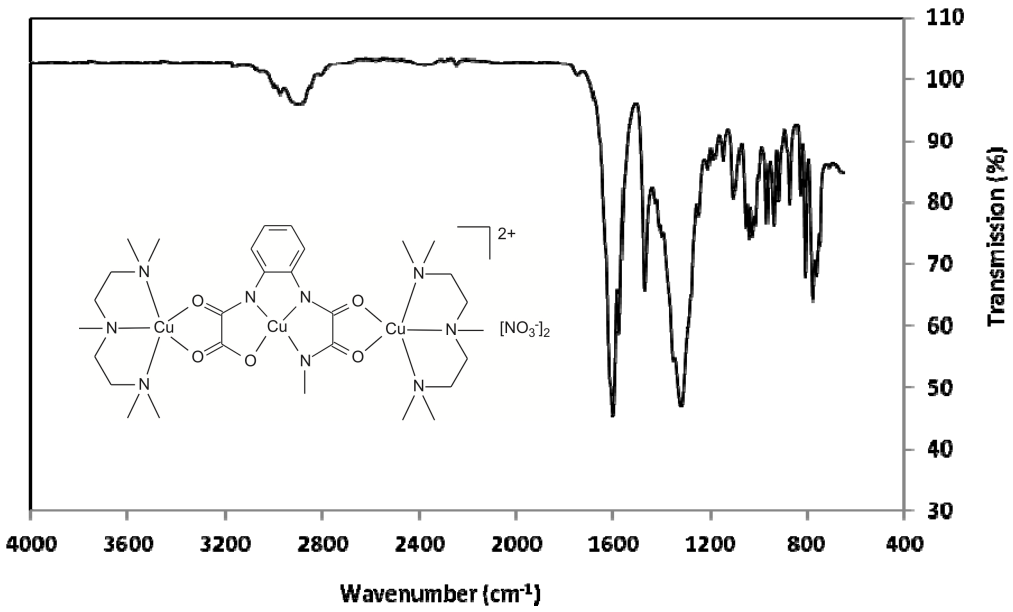

Fig. S5. IR spectrum of **5**.

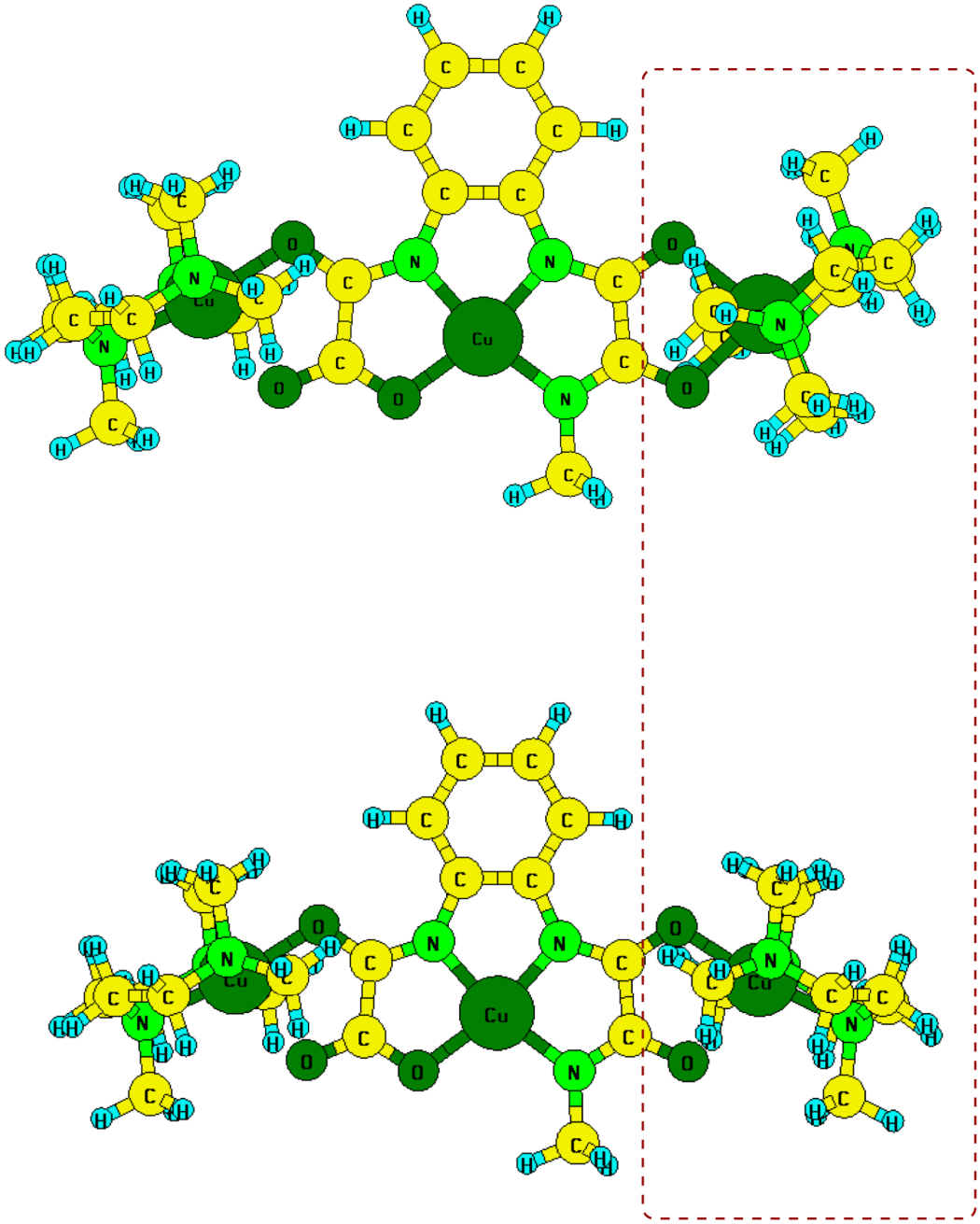

Fig. S6. Above: Schematic view of the molecular structure of geometry optimized **5A**. Below: Schematic view of the molecular structure of a geometry optimized conformer of **5A** having identical coordination geometries of the terminal $[Cu(pmdta)]^{2+}$ fragments.