MICROWAVE SYNTHESIS OF MULTIMETALLIC DITHIOLENE COMPLEXES WITH BRIDGING TETRATHIOOXALATE (TTO) LIGANDS AS PRECURSORS FOR MOLECULAR CONDUCTORS

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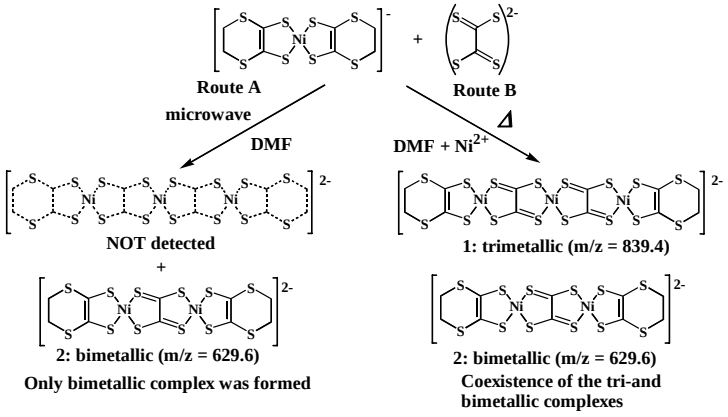
Multimetallic complexes with bridging tetrathiooxalate (tto) ligands have aroused a great deal of interest as molecular metals and superconductors.[1] The authors previously discovered versatile synthetic method which provides conducting trimetallic complexes with two tto ligands (**1**) in addition to bimetallic complexes (**2**) (Scheme 1: Route B).[2] Although **1** can be isolated and identified, **2** has not been separated due to the lability of **2** during HPLC separation. In this work, we found new selective preparation of the bimetallic complexes like **2** by the use of microwave. Products from the two reaction routes (A and B in Scheme 1) were followed up by the measurement of electrospray ionization mass spectrometry (ESI-Mass) in which a significant difference between the two was observed. For example, monometallic complex $(Bu_4N)[Ni(dddt)_2]$ (0.15 mmol) and $(Et_4N)_2(tto)$ (0.15 mmol) dissolved in *N*,*N*-dimetylformamide (25 ml) were poured into a pressure bottle. This solution was treated with microwave for 2 minutes and cooled down to r.t. This treatment was repeated 6 times (Scheme 1: Route A). Formation of the bimetallic $[(tto)Ni_2(dddt)_2]$ complex was detected (ESI-Mass *m*/z = 629.6). However, the trimetallic complex was not observed within the sensitivity of the ESI-Mass. The result quite differed from that of Route B reported in ref. 2. For metal complexes with ligands analogous to dddt, the similar results were observed. In this presentation, details of the synthetic conditions and ESI-Mass spectrometry in the above selective reactions with and without microwave will be discussed. The application of the products for molecular conductors will also be discussed



Scheme 1

References

1. Pullen, A. E.; Zeltner, S.; Olk, R.-M.; Hoyer, E.; Abboud, K. A.; Reynolds, J. R. *Inorg. Chem.* **1996**, *35*, 4420.
2. Kubo, K; Nakao, A.; Yamamoto, H. M.; Kato, R. *J. Am. Chem. Soc.* **2006**, *128*, 12358.