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# Structure and Coordination Behaviour of 1*H*-1,2,3-Triazole Ligands with a Dithiolene Backbone

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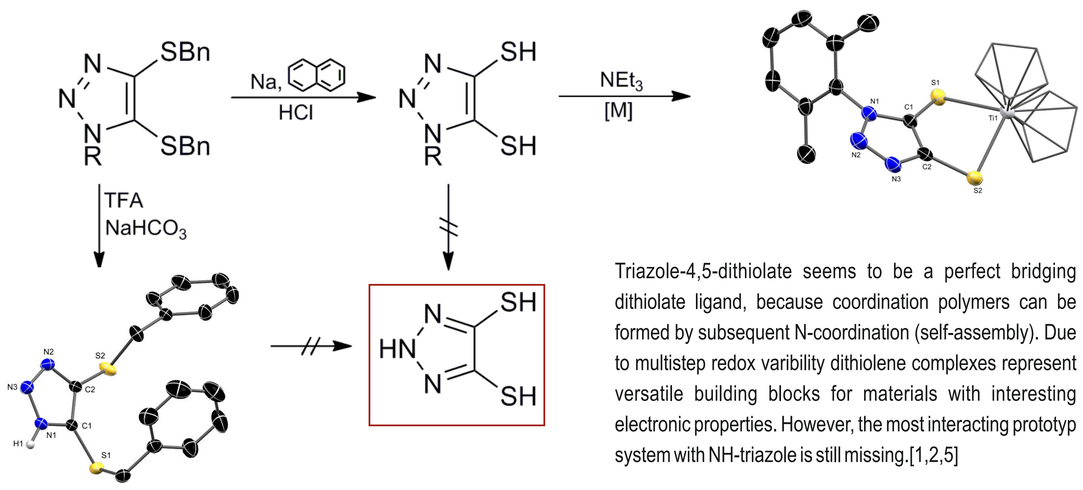
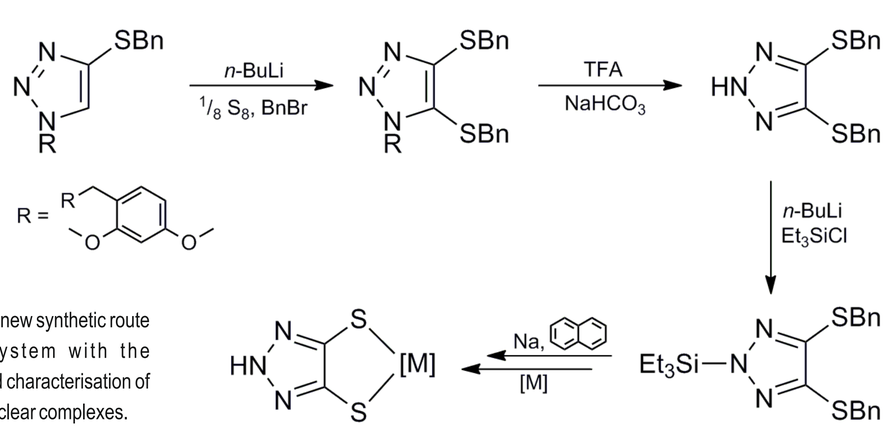
## Introduction



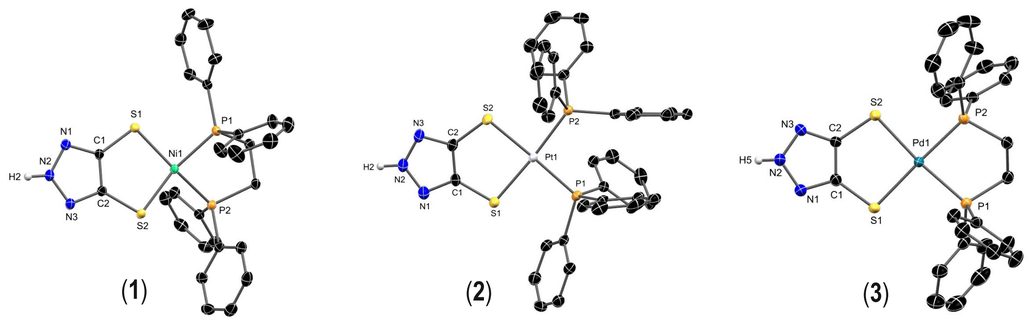

Triazole-4,5-dithiolate seems to be a perfect bridging dithiolate ligand, because coordination polymers can be formed by subsequent N-coordination (self-assembly). Due to multistep redox varibility dithiolene complexes represent versatile building blocks for materials with interesting electronic properties. However, the most interacting prototyp system with NH-triazole is still missing.[1,2,5]

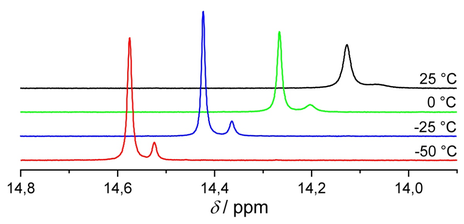
## Synthesis



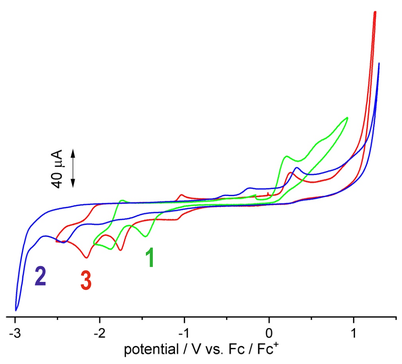

Here we show a new synthetic route to the NH system with the construction and characterisation of mono- to polynuclear complexes.

## Mononuclear complexes

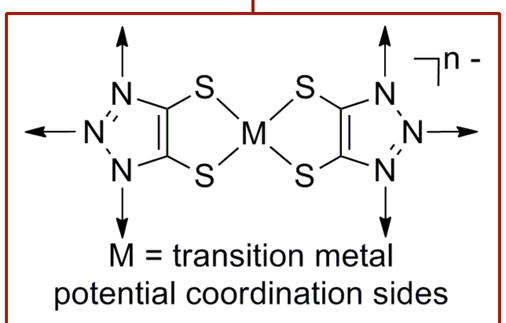


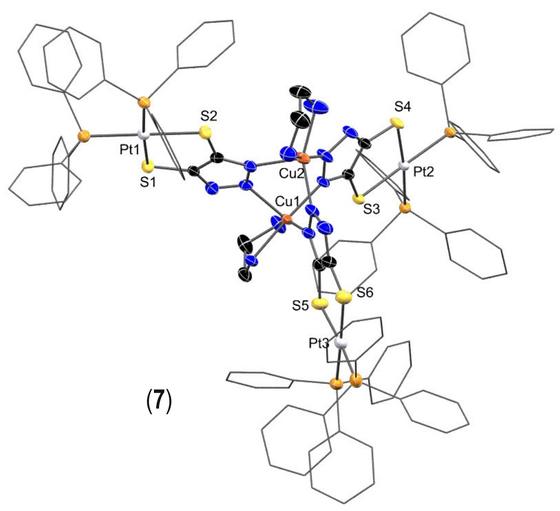

By variable temperature NMR studies with **2** two clear NH signals are visible at low temperature, which converge to a broad signal at 25 °C. At this temperature the exchange of protons at 1*H* and 2*H* position is fast.




In cyclic voltammetry measurements with **1**, **2** and **3**, irrev. oxidations at the ligand can be observed in the range of 0.35 V and reduction processes on the metal between -2.5 V and -1.8 V.[4]



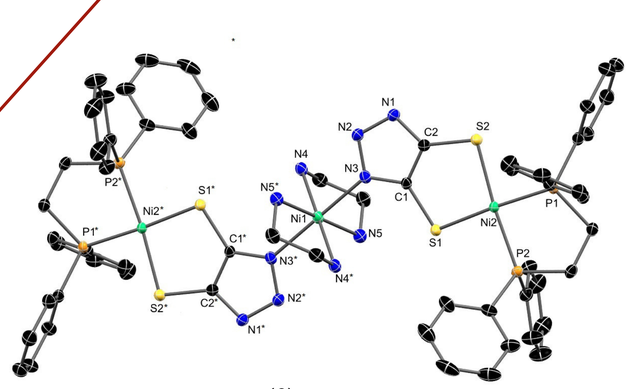

## Polynuclear complexes




By reacting the mononuclear complexes **1**, **2** or **3** with metal salts, polynuclear complexes can be assembled. Here, a dinuclear complex with $[CpFe(CO)_2Br]$ (**5**) and a trinuclear complex with $Ni(NO_3)_2$ could be synthesised from **1**. The complexes **2** and **3** form the pentinuclear complexes (**7**) and (**8**) with $Cu(NO_3)_2$. Apparently the triazole can adopt several coordination modes. The M-N bond lengths correspond to typical triazole M bonds.[6]

**Table 3**: Selected X-ray data from **5**, **6** and **7**

| | M-N [Å] |
|---|---|
| **5** | 1.956(3) |
| **6** | 2.106(3) |
| **7** | 2.124(5) / 1.986(6) |




## Bisdithiolene complexes

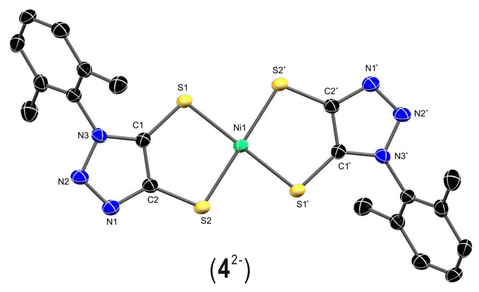
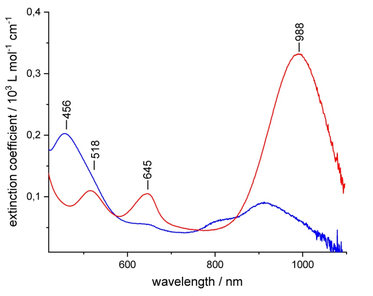



**Table 1**: Selected X-ray data from $\mathbf{4}^{2-}$ and $\mathbf{4}^{-}$

| | S2-C2[Å] | C1-C2 [Å] | M-S2 [Å] |
|---|---|---|---|
| **1** | 1.737(1) | 1.400(2) | 2.2007(5) |
| $\mathbf{4}^{2-}$ | 1.751(3) | 1.370(4) | 2.2139(7) |
| $\mathbf{4}^{-}$ | 1.728(4) | 1.373(5) | 2.1813(10) |
| $[Ni(t\text{-}Bu_2bdt_2)]^{2-}$ | 1.755(2) | 1.401(3) | 2.1715(9) |
| $[Ni(t\text{-}Bu_2bdt_2)]^{-}$ | 1.744(4) | 1.407(5) | 2.1400(12) |

The homoleptic complex $\mathbf{4}^{2-}$ was oxidised to the monoanion $\mathbf{4}^{-}$ in air. Interestingly, only the M-S bonds show a shortening known from literature. The mean descrease amounts to 1.4% for the $[Ni(t\text{-}Bu_2bdt_2)]^{2-/-}$ redox couple and 1.3% for $\mathbf{4}^{2-/-}$.[1,3]

The dianion ($\mathbf{4}^{2-}$,blue) shows a strong CT transition from $NiS_4$ to $\pi^*$(Xy) at 456 nm. Due to the oxidation to the monoanion ($\mathbf{4}^{-}$, red) an intense intervalence charge transfer band at 988 nm can be observed. This band could be assigned to a transition from the SOMO-1 to the SOMO orbital.[1]
The EPR spectrum of the monoanion shows a rhombic signal with g-value aniostropy being typical for a major oxidation in the dithiolene.[7]



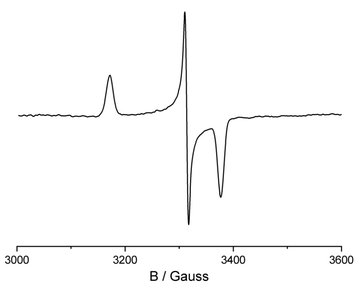
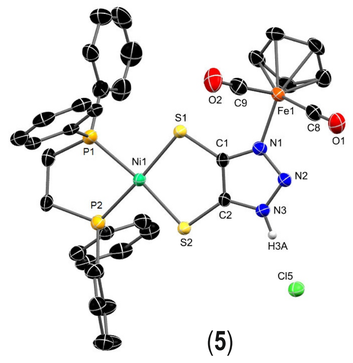




**Table 2**: g values of $\mathbf{4}^{-}$

| | $g_1$ | $g_2$ | $g_3$ | $\Delta g$ |
|---|---|---|---|---|
| $\mathbf{4}^{-}$ | 2.137 | 2.045 | 2.006 | 0.131 |
| $[Ni\{S_2C_2(CO_2Me)_2\}_2]]$ | 2.13 | 2.04 | 2.00 | 0.13 |




[1] D. Schallenberg, N. Pardemann, A. Villinger, W. W. Seidel, *Dalton Trans.* **2022**, *ASAP*.
[2] D. Schallenberg, PhD thesis, University of Rostock, **2013**.
[3] D. Sellmann, H. Binder, D. Häußinger, F. W. Heinemann, J. Sutter, *Inorg. Chim. Acta* **2000**, *300-302*, 829-836.
[4] L. Zabojnik, BSc thesis, University of Rostock, **2021**.
[5] N. Pardemann, MSc thesis, University of Rostock, **2019**.
[6] M. Y. Antipin, G. G. Aleksandrov, Y. T. Struchkov, Y. A. Belousov, V. N. Babin, N. S. Kochetkova, *Inorg. Chim. Acta* **1983**, *68*, 229-232; C. R. Maldonado, C. Marin, F. Olmo, O. Huertas, M. Sánchez-Moreno, M. J. Rosales, J. M. Salos, *J. Med. Chem.* **2010**, *53*, 6964-6972; D. V. Davydov, V. V. Chernyshev, V. B. Rybakov, Y. F. Oprunenko, I. P. Beletskaya, *Mendeleev Commun.* **2018**, *28*, 287-289.
[7] A. Begum, G. Moula, S. Sarkar, *Chem. - Eur. J.* **2010**, *16*, 12321-12327.

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