Universität Rostock Traditio et Innovatio

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

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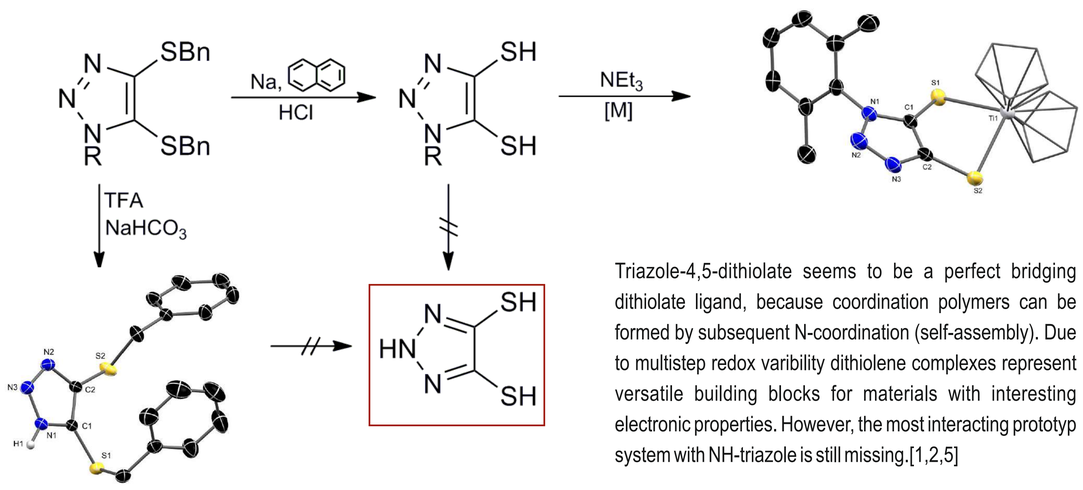
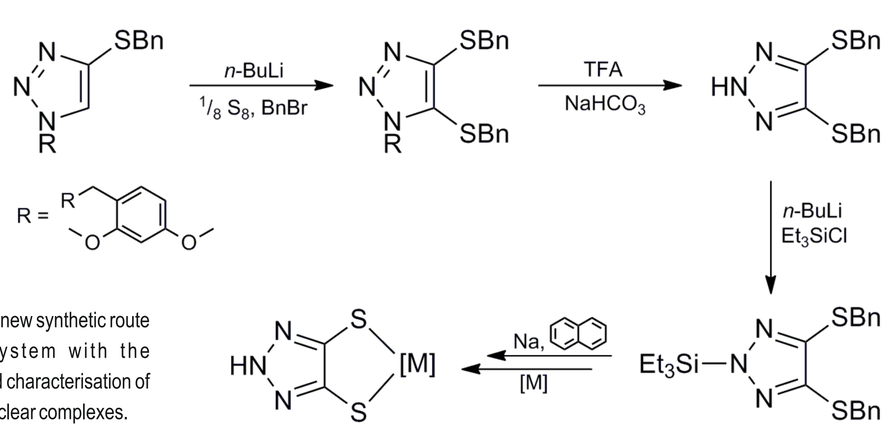
Introduction



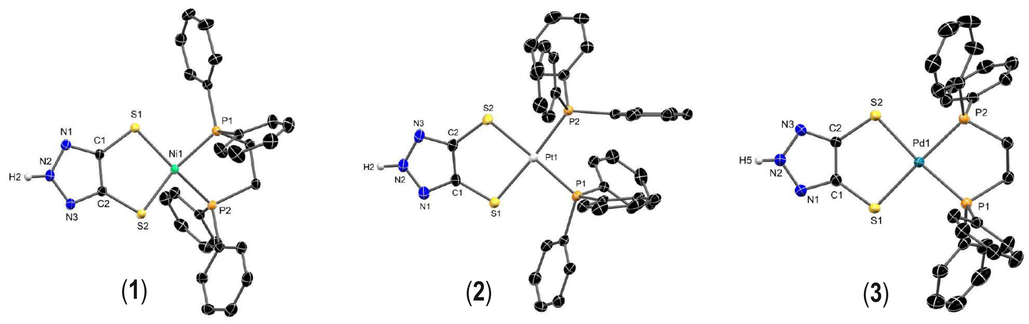
Triazole-4,5-dithiolate seems to be a perfect bridging dithiolate ligand, because coordination polymers can be formed by subsequent N-coordination (self-assembly). Due to multistep redox varibility dithiolene complexes represent versatile building blocks for materials with interesting electronic properties.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

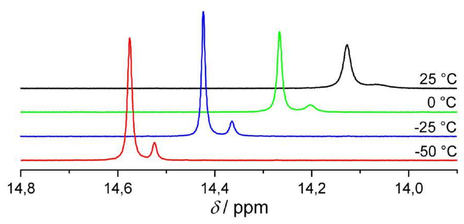
Synthesis



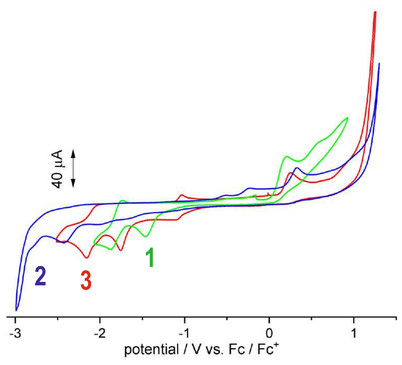
Here we show a new synthetic route to the NH system with the construction and characterisation of mono- to polynuclear complexes.

Mononuclear complexes

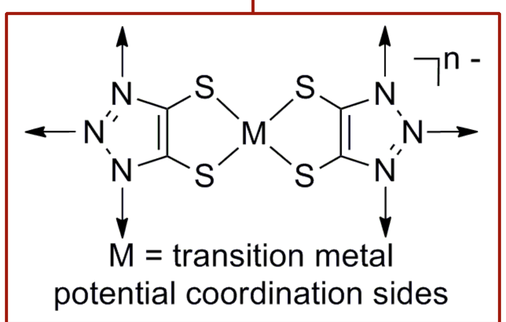




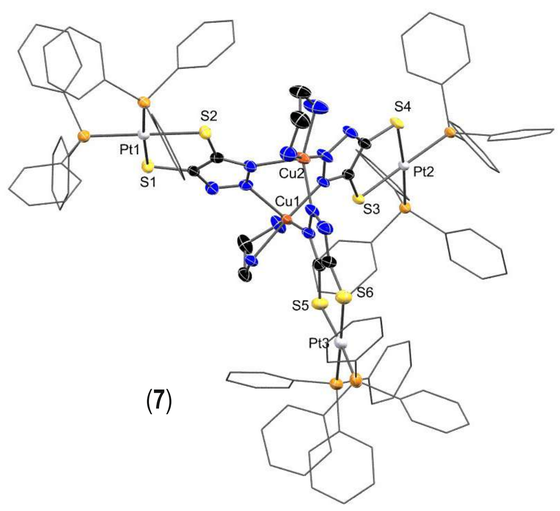
By variable temperature NMR studies with **2** two clear NH signals are visible at low temperature, which converge to a broad signal at 25 °C. At this temperature the exchange of protons at 1*H* and 2*H* position is fast.



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]



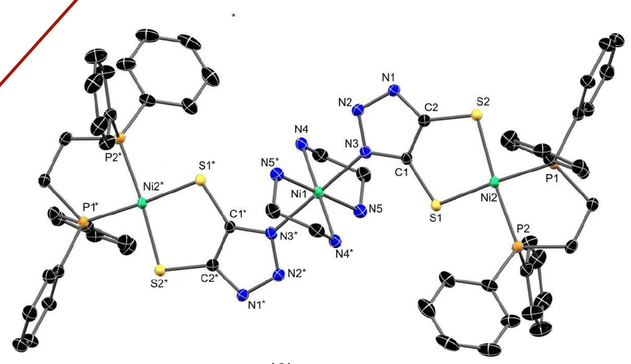
Polynuclear complexes



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

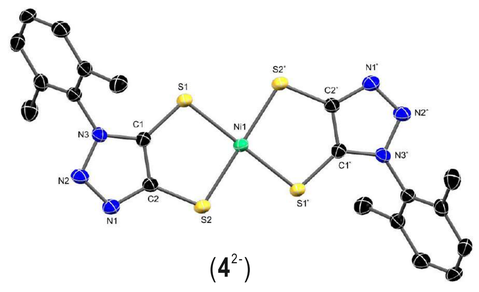


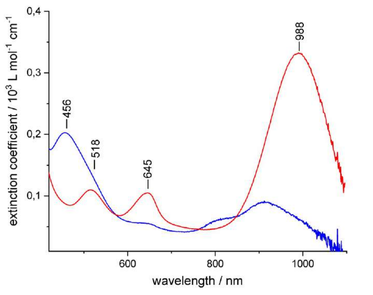
Table 1: Selected X-ray data from $\mathbf{4}^{2-}$ and $\mathbf{4}^{-}$

	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 π^*(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]



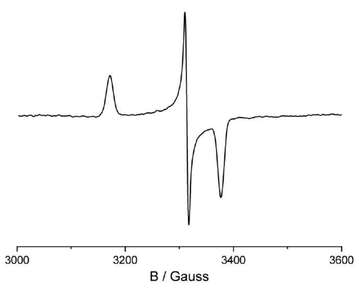
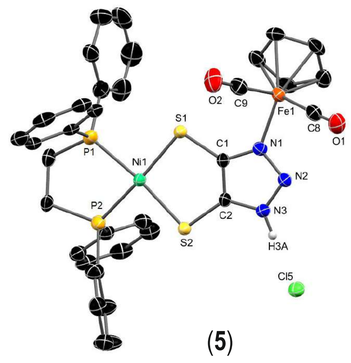


Table 2: g values of $\mathbf{4}^{-}$

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



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