

Synthesis of Novel Metal Complexes of the 1,2-Dithiolene Ligand, 1,2,5-Thiadiazole-3,4-dithiol: Precursors to New Molecular Conductors

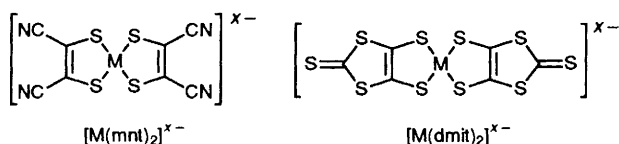
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Complexes of the ligand 1,2,5-thiadiazole-3,4-dithiol have been prepared; their spectroscopic and electrochemical properties show that they are potentially of use in preparing conducting materials.

The past 20 years has seen the development of a new class of materials, namely molecular 'metals' and superconductors. One important class of compounds in this area has contained multisulphur π acceptors based on transition metal bis-dithiolene complexes. These studies have concentrated on metal complexes of maleonitriledithiol (H_2mnt) and 4,5-mercapto-1,3-dithiole-2-thione (H_2dmit) with the metals Ni, Pd and Pt. Using a suitable choice of the central metal and the counter cation, compounds have been prepared which display high room temperature conductivities and metallic behaviour.¹

For example, $Na[Ni(dmit)_2]_2$ remains metallic down to 25 K² and $(Me_4N)[Ni(dmit)_2]_2$ ³ has been shown to become superconducting under 7 kbar pressure at 5 K. In these



$$(0 \leq x \leq 1)$$

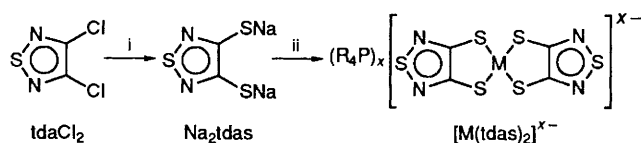
compounds the Peierls instability associated with a low-dimensional metal is suppressed owing to extensive intermolecular interactions between the sulphur atoms.

In an attempt to extend the range of metal complexes displaying novel optical, magnetic or electrical conduction

Table 1 Spectroscopic properties of nickel complexes of the tdas ligand^a

Complex	IR, ν/cm^{-1}	Near-IR, λ/nm ($10^{-4} \epsilon/\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$)	UV, λ/nm ($10^{-4} \epsilon/\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$)
$(\text{Bu}_4\text{P})_2[\text{Ni}(\text{tdas})]$	487 ms, br	—	225 (2.6)
			317 (4.4)
			435 (1.3)
$(\text{Bu}_4\text{P})[\text{Ni}(\text{tdas})]$	4000–3500	930 (1.4)	220 (2.4)
		2306 (0.61)	315 (3.9)
		2354 (0.70)	360 (1.5)
		2404 (1.1)	440 (0.94)

^a Satisfactory elemental analyses were obtained.



Scheme 1 M = Ni, Pd, Pt or Cu, $x = 2$
 M = Fe, $x = 1$
 R = Buⁿ or Ph

Reagents and conditions: i, 2Na₂S·9H₂O; ii, R₄PBr, then MCl₂

properties, we have synthesised the first metal complexes of the ligand 1,2,5-thiadazole-3,4-dithiol (H₂tdas) first characterised by Rees⁴ and more recently synthesised by Wolmershäuser and Johann.⁵ The presence of peripheral nitrogen atoms on the ligand may enhance intermolecular interactions in the solid state by the presence of S···N as well as S···S interactions. The complexes were synthesised from aqueous solutions of the disodium salt of the free ligand as shown below in Scheme 1.

Chemical oxidation of the dianionic Ni complex with tetracyanoquinodimethane (tcnq) leads to the monoanionic complex. Spectroscopic details of (Bu₄P)₂[Ni(tdas)₂] and (Bu₄P)[Ni(tdas)₂] are given in Table 1. An important feature of the near-IR spectrum of the monoanionic complex is the presence of broad, high intensity absorption bands which occur both in solution and in the solid state. Cyclic voltammetry of the Ni complex in MeCN using an Ag/AgCl reference

electrode shows a quasi-reversible one-electron oxidation at $E = +0.95$ V.

Electrooxidation of acetonitrile solutions of tetrathiafulvalene (tff) in the presence of (Bu₄P)[Ni(tdas)₂] resulted in an anodic growth of black crystals of composition [tff]₂[Ni(tdas)₂]. Four-probe conductivity measurements on a compressed disc of this material exhibited semiconducting behaviour with a band gap of 340 meV and a room temperature conductivity of 0.1 S cm⁻¹.

The results to date show that complexes of the tdas ligand exhibit many properties similar to those of the mnt and dmit complexes. Full characterisation of these and other metal complexes of tdas, their partially oxidised derivatives and X-ray crystallographic studies will be presented in future papers.

We thank the SERC for support.

Received, 19th July 1990; Com. 0/03262J

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