

First X-Ray Structure of a Monoanionic Nickel Complex of 1,2,5-Thiadiazole-3,4-dithiolate

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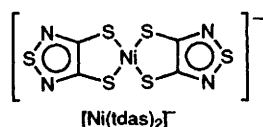
The crystal structure of the title complex contains monoanion dimeric pairs in a staggered arrangement, in contrast to the structure reported for the corresponding dianion in which the anions are isolated.

In recent years there have been extensive studies of metal complexes of multisulfur π -acceptor ligands because of their capacity to form molecular metals and superconductors and more recently because of their promising third-order non-linear optical properties.^{1,2} As part of our work to extend the range of metal complexes exhibiting these technologically important properties we reported the synthesis of the first metal complexes of the ligand 1,2,5-thiadiazole-3,4-dithiol (H_2tdas).³ Recently Cassoux and coworkers have reported the crystal structures of two dianion $[Ni(tdas)_2]^{2-}$ salts.⁴ We now report the first crystal structure of a monoanionic complex of this ligand, $[PBu_4][Ni(tdas)_2]$, together with a further study of its properties.

$[PBu_4]_2[Ni(tdas)_2]$ was prepared as described previously.^{3,4} $[PBu_4][Ni(tdas)_2]$ was prepared by adding slowly a solution of I_2 (0.15 g, 0.6 mmol) in degassed acetone to a solution of $[PBu_4]_2[Ni(tdas)_2]$ (1.26 g, 1.5 mmol) under nitrogen. The reaction mixture was stirred for a further 30 min after which time the solution was evaporated to ca. 15 ml. Methanol was added to yield black shiny needles which were filtered off and

washed with methanol, yield: 0.65 g (90.7%). Elemental analyses were satisfactory.

The crystal structure[†] of $[PBu_4][Ni(tdas)_2]$ contains monoanion dimer pairs as shown in Fig. 1. This is in contrast to the structure of the corresponding dianion in which the anions are isolated from one another. Within the dimer pairs the molecules are staggered relative to one another in such a way that the sulfur atom of one of the ligands in one anion forms a bond to the nickel atom of the other anion of the dimer pair. The sulfur-over-metal arrangement has been observed previously for monoanion nickel dithiolene complexes.⁵ Within the monoanion the Ni-S bond distances in which the S atoms are not involved in intradimer interactions are around 2.22 Å whereas the Ni-S bond in which the Ni is involved in



[†] Crystal data: $[PBu_4][Ni(tdas)_2]$, $C_{20}H_{36}N_4NiPS_6$, $M = 614.57$, $a = 9.746(3)$, $b = 19.730(3)$, $c = 15.441(2)$ Å, $\beta = 98.07(2)^\circ$, $V = 2940(1)$ Å³, space group $P2_1/n$, $Z = 4$, $D_c = 1.388$ g cm⁻³, $\mu(Mo-K\alpha) = 11.42$ cm⁻¹. Data were collected at 25 °C on a Rigaku AFC5R diffractometer using Mo-K α radiation using the ω -2 θ scan technique to a maximum 2θ value of 55.1°. The structure was solved by direct methods to give $R = 0.056$ from 6986 unique reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

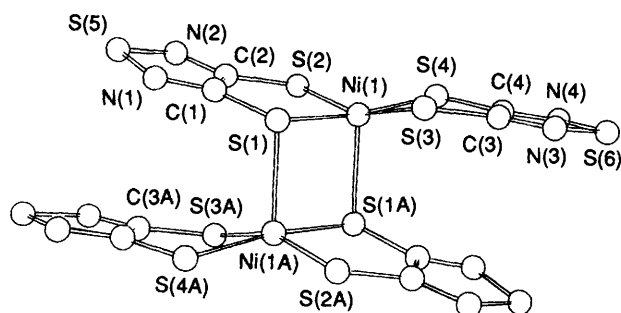


Fig. 1 Structure of monoanion dimer pairs in $[\text{PBu}_4][\text{Ni}(\text{tdas})_2]$

intradimer interactions is somewhat shorter at 2.207 Å. The intradimer Ni–S distance of 2.385 Å is only slightly longer than the N–S distances within the anion.

A comparison of the bond distances in $[\text{Bu}_4\text{N}][\text{Ni}(\text{tdas})_2]$ with those reported for the corresponding $[\text{Bu}_4\text{N}]_2[\text{Ni}(\text{tdas})_2]$ show almost no change in the S–C or C–N distances, but the C–C and S–N distances are slightly shorter in the dianion. The N–S distance of 2.209 Å in the dianion is considerably shorter than the Ni–S distance in the monoanion. The relatively small changes in bond distances observed on going from the dianion to the monoanion are consistent with the bonding in these compounds in which the additional electron in the dianion is added to a $3b_{2g}$ molecular orbital which is delocalised over the dianion. It is significant that all the distances within the thiadiazole ring are intermediate between those expected for single and double bonds indicating that there is extensive delocalisation within the ring in these metal complexes. In the dianion salt the anion is centrosymmetric and essentially planar with the atomic deviations from the average plane not exceeding 0.001 Å. However, in the monoanion salt the effect of the interdimer Ni–S bond is to destroy the centrosymmetric nature of the anion so that the complex exhibits a mean deviation from the plane of 0.2115 Å.

Cyclic voltammetry studies of $[\text{Bu}_4\text{P}][\text{Ni}(\text{tdas})_2]$ in methyl cyanide using a saturated calomel reference electrode show an irreversible oxidation at +0.87 V. This presumably corresponds to the formation of the neutral complex and is irreversible owing to the insoluble nature of the product. Further studies are in progress to prepare and characterise the neutral complex.

As reported previously $[\text{Bu}_4\text{P}][\text{Ni}(\text{tdas})_2]$ exhibits a strong absorption band in the near IR corresponding to the $2b_{1u}$ to $3b_{2g}$ transition commonly found in monoanion dithiolenes.² The solid state reflectance spectra of the monoanion however shows a very broad intense band stretching from around 1000 to beyond 2300 nm. This difference between the solution and solid state spectra probably implies that in solution the monoanion exists as an isolated species and only forms the dimeric species in the solid state. Monoanionic dimers of the type found in this compound may exhibit triplet–singlet behaviour as a function of temperature.⁶ Detailed magnetic studies are in progress.

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