The Synthesis and First X-Ray Structures of Nickel Complexes of 1,2,5-Thiadiazole-3,4-dithiolate

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The $(R_4N)_2[Ni(tdas)_2]$ complexes ($tdas^{2-}$ = 1,2,5-thiadiazole-3,4-dithiolate and R = Bu, Et) are prepared and characterized by X-ray crystallography, which reveals differences in their structure dependant on the size of the R_4N cation.

Bis-1,2-dithiolene metal complexes have aroused a great deal of interest as precursors for molecular metals and even superconductors.[1–3] Recently, attempts have been made to extend the range of metal complexes exhibiting conducting properties, which concern the first synthesis of $[M(tdas)_2]^{n-}$ anion complexes (Fig. 1; $tdas^{2-}$ = 1,2,5-thiadiazole-3,4-dithiolate) in different oxidation states.[4] They have been isolated as their salts with tetraalkyl- and tetraphenyl-phosphonium cations, or with the TTF (tetrathiafulvalene) cation. However, the procedure for their synthesis has been described only schematically, and their crystal structures have not yet been determined. Here, we report a detailed procedure for preparing the $(R_4N)_2[Ni(tdas)_2]$ complexes (R = Bu and Et), as well as their X-ray crystal structures.

$Na_2(C_2N_2S_3)$ was prepared by adding dropwise, over 2 h, a solution of 3,4-dichloro-1,2,5-thiadiazole (9.1 g, 0.059 mol) in

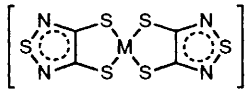

Fig. 1 The $[M(tdas)_2]^{n-}$ anion complexes

ethanol (50 ml) to a solution of $Na_2S\cdot9H_2O$ (29 g, 0.12 mol) in aqueous alcohol (400 ml ethanol and 150 ml H_2O). The resulting solution slowly turned yellow, and after 2 h stirring, was evaporated to dryness at < 45 °C to prevent polymerization. The residue was extracted with ethanol (3 × 100 ml) and the combined extracts were evaporated to dryness. The resulting highly hydroscopic yellow–orange solid $Na_2(C_2N_2S_3)$ was dried over KOH under vacuum (yield: 6.9 g, 60%).†

$(Et_4N)_2[Ni(tdas)_2]$ was prepared by adding dropwise a solution of $NiCl_2\cdot6H_2O$ (3.19 g, 0.0134 mol) in methanol (30 ml) to a solution of $Na_2(C_2N_2S_3)$ (5.2 g, 0.0268 mol) in methanol (50 ml). After stirring for 1 h, the resulting solution was filtered off and added dropwise to a stirred solution of Et_4NBr (5.64 g, 0.0268 mol) in methanol (30 ml). A precipitate formed and was filtered off, washed with methanol, water and diethyl ether and air dried (yield: 4.48 g, 55%).† Black square bipyramidal crystals (m.p. 181–183 °C), suitable for X-ray analysis were obtained by recrystallization from methanol.‡

Likewise, $(Bu_4N)_2[Ni(tdas)_2]$ was prepared by adding dropwise a solution of $NiCl_2\cdot6H_2O$ (2.8 g, 0.018 mol) in methanol (50 ml) to a solution of $Na_2(C_2N_2S_3)$ (5.2 g, 0.0268 mol) in methanol (50 ml). After stirring for 30 min, the resulting solution was filtered and added dropwise to a vigorously stirred solution of Bu_4NBr (8.63 g, 0.0268 mol) in methanol (50 ml). Then, H_2O (30 ml) was added and the methanol was distilled using a rotary evaporator. The resulting precipitate was filtered off, washed with aqueous ethanol (1 : 1), diethyl ether and air dried (yield: 5.8 g, 59%).† Greenish needle-like crystals (m.p. 143–144 °C), suitable for X-ray analysis were obtained by recrystallization from aqueous ethanol.‡

The $(Et_4N)_2[Ni(tdas)_2]$ crystals have a layered structure, in which cation and anion layers are parallel to the *ab* plane and alternate along the *c* axis (Fig. 2). The anion layer is composed of centrosymmetric, essentially planar $[Ni(tdas)_2]^{2-}$ dianions

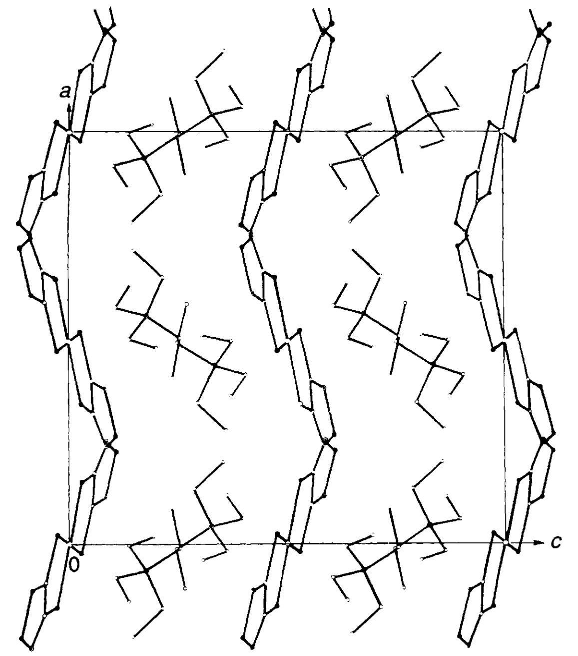

Fig. 2 Projection of the $(Et_4N)_2[Ni(tdas)_2]$ crystal structure on the *ac* plane

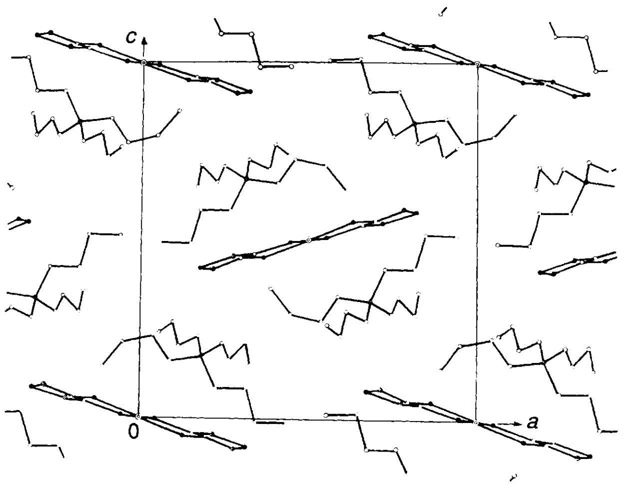

Fig. 3 Projection of the $(Bu_4N)_2[Ni(tdas)_2]$ crystal structure on the *ac* plane

(the atomic deviations from the averaged plane do not exceed 0.001 Å). The Ni atom has a square-planar coordination. The Ni–S bond lengths are 2.200(1) and 2.199(1) Å. The $(Et_4N)^+$ cations occupy general positions in the crystal. The coordination geometry around the N atom (interatomic distances and bond angles) are all characteristic of the tetrahedral Et_4N^+ cation.[7] The $(Bu_4N)_2[Ni(tdas)_2]$ crystal structure (Fig. 3) consists of a much looser packing of $[Ni(tdas)_2]^{2-}$ dianions, which occupy special centrosymmetric positions, the Bu_4N^+ cations filling holes between the anions. The square-planar configuration of the Ni–S bonds is determined by the Ni atom location on the symmetry centre. The $[Ni(tdas)_2]^{2-}$ dianion again shows an approximately planar geometry (the atomic deviations from the averaged plane are less than 0.05 Å). The values of the bond lengths and angles of the Bu_4N^+ cation correspond to those observed in $(R_4N)_2[Ni(dmt)_2]$.[8,9]

Therefore, the $(Et_4N)_2[Ni(tdas)_2]$ and $(Bu_4N)_2[Ni(tdas)_2]$ salts have different crystal structures, which are probably determined by the cation size. The smaller size of the Et_4N^+ cation allows a layered packing in $(Et_4N)_2[Ni(tdas)_2]$ in contrast to the mixed ion packing observed in $(Bu_4N)_2$[Ni-

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† All compounds gave satisfactory microanalyses and the expected IR spectra.

‡ *Crystal data* $(Et_4N)_2[Ni(tdas)_2]$. $C_{20}H_{40}N_6NiS_6$, M = 615.6, orthorhombic, space group *Pbca*, a = 13.673(5), b = 13.890(5), c = 15.101(6) Å, V = 2868.0(8) Å^3, Z = 4, D_c = 1.42 g cm^{-3}, μ(Cu-Kα) = 1.541 Å. Data were collected at room temperature on a DAR-UM diffractometer using graphite-monochromated Cu-Kα radiation. The unit cell dimensions were determined by least-squares refinement based on the setting angles of 25 well-centred reflections. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was applied in the DIFABS procedure. The structure was solved by direct methods followed by successive Fourier synthesis and full-matrix least-squares refinement using the SHELX-76, SHELX-86 program systems,[5] all non-hydrogen atoms being refined anisotropically, to give R = 0.046 for 1929 independent reflections [$I \geqslant 2\sigma(I)$].

$(Bu_4N)_2[Ni(tdas)_2]$. $C_{36}H_{72}N_6NiS_6$, M = 840.1, monoclinic, space group $P2_1/n$, a = 14.684(6), b = 9.813(6), c = 15.895(4) Å, γ = 94.9(4)°, V = 2281.0(8) Å^3, Z = 2, D_c = 1.31 g cm^{-3}, μ(Mo-Kα) = 0.711 Å. Data were collected at room temperature on a Kuma Diffraction diffractometer using graphite-monochromated Mo-Kα radiation. No absorption correction was applied. The structure was solved as above, but using the AREN-88 program system,[6] to give R = 0.040 for 616 independent 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.

Table 1 Bond lengths (d) in metal cycles of dianion nickel complexes with the tdas^{2-},[a] dmit^{2-},[b] dmt^{2-}[c] and mnt^{2-}[d] ligands

	d/Å			
Compound	Ni–S	S–C	C–C	Ref.
$(Et_4N)_2[Ni(tdas)_2]$	2.200(1)	1.724(5)	1.439(6)	This work
$(Bu_4N)_2[Ni(tdas)_2]$	2.209(3)	1.72(1)	1.47(2)	This work
$(Bu_4N)_2[Ni(dmit)_2]$	2.216(6)	1.75(2)	1.39(2)	8
$(Bu_4N)_2[Ni(dmt)_2]$	2.188(4)	1.70(1)	1.42(2)	9
$(Me_4N)_2[Ni(mnt)_2]$	2.166(6)	1.75(2)	1.33(2)	10

[a] 1,2,5-Thiadiazole-3,4-dithiolate. [b] 1,3-Dithiole-2-thione-4,5-dithiolato. [c] 1,2-Dithiole-3-thione-4,5-dithiolato. [d] 2,3-Dimercaptobut-2-enedinitrile.

$(tdas)_2]$, where bulky Bu_4N^+ cations fill the holes between the anions, as was previously observed in the parent $(Bu_4N)_2$-$Ni(dmit)_2]$.[8] However, comparison of bond lengths in the $Ni(tdas)_2$ metal cycles leads to the conclusion that they are identical, within standard deviations, for both $(Et_4N)_2[Ni(tdas)_2]$ and $(Bu_4N)_2[Ni(tdas)_2]$ complexes (Table 1), *i.e.* they are not cation-dependent and are determined by the anion charge only, *cf.* other bis-1,2-dithiolene complexes.[11,12] It is also interesting to note that the tdas complexes show metal cycle bond lengths similar to those observed in the dmit and dmt complexes,[8,9] but different from those observed in the mnt complexes.[10]

In conclusion, like the $(R_4N)_2[M(dmit)_2]$ parent complexes,[1] both $(R_4N)_2[Ni(tdas)_2]$ complexes may be used for the preparation of partially oxidized conducting compounds, and the differences in the structures of these precursor complexes when R = Et or Bu may possibly result in striking differences in the structural and electrical properties of derived conducting species.

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