$[ET]_3[NiCl_4]\cdot H_2O$; a Metallic Conductor containing the $NiCl_4{}^{2-}$ Anion in a Distorted Square Planar Geometry [ET = bis(ethylenedithio)tetrathiafulvalene]

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The title compound is a metallic conductor at room temperature and its crystal structure reveals that the $NiCl_4{}^{2-}$ anions are not tetrahedral but have a unusual distorted square planar geometry not previously reported; the $NiCl_4{}^{2-}$ anions are sandwiched between lamelli of ET cations.

The effect of the geometry of the anion upon the structure and properties of charge-transfer salts of, for example, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) is the subject of continuing interest for a number of groups[1,2]. However, the effect of the cation upon the geometry of the anion itself is not normally considered to be significant. As part of a study of charge transfer compounds of ET we have prepared $[ET]_3[NiCl_4]\cdot H_2O$ **1**. In the solid state this material behaves as a conductor at room temp. (20 S cm^{-1}). As the temperature is decreased the conductivity increases to a plateau at *ca.* 150 K and then decreases to semi-metallic behaviour down to 20 K (σ *ca.* 12 S cm^{-1}). The crystal structure of **1**† reveals a stacked sheet structure comprising of layers that contain three crystallographically independent ET cations (Fig. 1). The mean interplanar separation of the sheets is *ca.* 3.6 Å, whilst within individual sheets the non-bonded S···S contacts are in the range 3.34–3.80 Å. The molecules pack to form a lamellar structure with the $NiCl_4{}^{2-}$ anions interposed between adjacent stacks and lying within the (010) plane. The geometry of the $NiCl_4{}^{2-}$ anion is unique. This anion is usually tetrahedral with only small distortions from normal tetrahedral angles (a search of the CSSR database[3] reveals a range of Cl–Ni–Cl angles in $NiCl_4{}^{2-}$ of 104–121°). In the structure of **1** we observe a geometry (Fig. 2) that more closely approaches square planar; the chlorine atoms lying within 0.6 Å of the $NiCl_4$ mean plane (the nickel atom lies on this plane). The Ni–Cl bond lengths are normal but the *trans*-Cl–Ni–Cl angles are 149.9(1) and 150.0(1)° whilst the *cis* angles are in the range 92.4(1)–95.2(1)°. The reason for this unusual geometry for the anion cannot be readily quantified, though there are a number of significant intermolecular contacts. Pairs of $NiCl_4{}^{2-}$ anions are linked by hydrogen bonds through pairs of water molecules to form dimer like units [Cl(4)····O(1) 3.19, Cl(3′)····O(1) 3.33 Å, Cl····O····Cl 127°]. Furthermore, there are short anion-cation Cl····S interactions that range between 3.38–3.65 Å as well as long range interactions (3.8–3.9 Å) that involve all four chlorine atoms. Clearly, these interactions

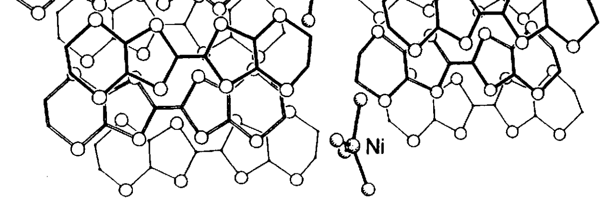

Fig. 1 Part of the lamellar structure of **1**. The sulfur atoms are depicted by open circles. Three layers of ET cations are shown; those at the 'top' are drawn with solid bonds, those in the 'middle' with open bonds and those at the 'bottom' with line bonds. The hydrogen bonds between pairs of $NiCl_4{}^{2-}$ anions and included water molecules are depicted by dashed bonds.

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† *Crystal data* **1**, $3[C_{10}H_8S_8]NiCl_4\cdot H_2O$: M = 1372.6, triclinic, a = 9.016(2), b = 16.269(3), c = 16.696(2) Å, α = 96.87(1) β = 93.22(1), γ = 90.81(2)°, U = 2427 Å^3, space group $P\bar{1}$, Z = 2, D_c = 1.88 g cm^{-3}. Crystal dimensions 0.10 × 0.10 × 0.36 mm, μ(Cu-Kα) = 125 cm^{-1}, λ = 1.54178 Å, $F(000)$ = 1388. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structure was solved by the heavy atom method and refined anisotropically using absorption corrected data to give R = 0.066, R_W = 0.066 for 4808 independent observed 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.

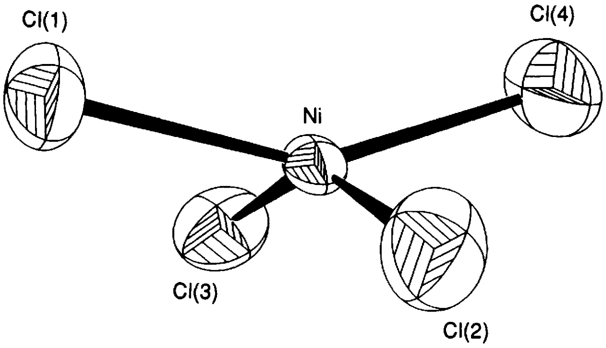

Fig. 2 X-Ray structure (50% probability ellipsoids) of the $NiCl_4^{2-}$ anion in **1**. Bond lengths (Å) and angles (°): Ni–Cl(1) 2.266(2), Ni–Cl(2) 2.244(3), Ni–Cl(3) 2.244(3), Ni–Cl(4) 2.279(3); Cl(1)–Ni–Cl(2) 93.9(1), Cl(1)–Ni–Cl(3) 92.4(1), Cl(2)–Ni–Cl(4) 93.9(1), Cl(3)–Ni–Cl(4) 95.2(1), Cl(2)–Ni–Cl(3) 149.9(1), Cl(1)–Ni–Cl(4) 150.0(1).

must play a part in determining the severe distortions from normal tetrahedral geometry observed in the anion.

This work underlines the importance of considering not only the stacking of the ET units in terms of the resulting conductivities but also the influence of these units upon the anions; clearly the cation–anion interactions are cooperative. A full analysis of the stacking motif, conductivity properties and band theory calculations will be reported in due course.[4]

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