Crystal engineering of metal complexes based on charge-augmented double hydrogen-bond interactions between thiosemicarbazides and carboxylates

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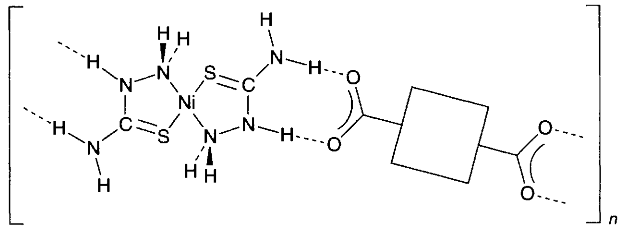
Charge augmented double hydrogen bonds have been used for the first time to form extended linear polymers between bis(thiosemicarbazide)nickel(2+) and dicarboxylate anions; the X-ray crystal structures of $[Ni(tsc)_2]^{2+}[tere]^{2-}$ 1 and $[Ni(tsc)_2(OH_2)_2]^{2+}[fum]^{2-}$ 2 [tsc = thiosemicarbazide, $H_2NC(S)NHNH_2$; tere = terephthalate, $C_6H_4(CO_2^-)_2$-1,4; fum = fumarate, *trans*-$^-O_2CCH{=}CHCO_2^-$] are discussed

Considerable interest has been shown recently in using complementary hydrogen-bond interactions as part of the design strategy for the development of new solid-state materials.[1–3] Varying both the number and arrangement of hydrogen-bond donors and acceptors, and steric factors can influence the solid-state structure significantly. Whitesides[4,5] and Lehn[6] and their coworkers have exploited the triple hydrogen-bond interactions between derivatives of barbituric acid and 2,4,6-triaminopyrimidine to give infinite linear or crinkled tapes or discrete 3 + 3 rosettes, depending upon the substituents on the two components.

The incorporation of metal ions into hydrogen-bonded extended arrays[7] has received less attention although such systems may have interesting magnetic, optical and conductivity properties. We have previously explored triple hydrogen-bond interactions between bis(dithiobiureto)nickel and a number of compounds containing the complementary ADA (A = hydrogen bond acceptor, D = hydrogen bond donor) arrangement[8,9] and also between bis(phosphine)platinum orotate complexes and organic substrates containing the complementary DAD arrangement[10] to give discrete aggregates, tapes and sheets.

Theoretical calculations[11] and experimental data[12] have indicated that the hydrogen-bonding interactions between two molecules where all of the donor sites (D) are localised on one component and acceptor sites (A) on the second (*i.e.* DDD≡AAA) are stronger than those where the donor and acceptor sites are distributed between the two molecules (*i.e.* ADA≡DAD or AAD≡DDA). The four repulsive secondary interactions[11] in ADA≡DAD reduce the total bonding energy to approximately the same as that in the double hydrogen-bonded system DD=AA, which has just two hydrogen bonds but only attractive secondary interactions. Hamilton and coworkers have used both thioureas[13,14] and guanidinium salts[15] as the basis of receptors for dicarboxylates and phosphodiesters, forming discrete 1 : 1 units that are stable even in competitive solvents. A number of crystal structures containing such double hydrogen bonds have been reported,† some of which contain metals.[16,17] This paper describes for the first time the design, synthesis and characterisation of infinite DD=AA hydrogen-bonded chains based on metal complexes.

Thiosemicarbazide is an attractive bifunctional ligand with a bidentate metal coordination mode and a thiourea unit possessing two hydrogen atoms in the correct orientation to hydrogen bond to a carboxylate anion. Therefore, a bis(thiosemicarbazide) complex with a 2+ charge and a rigid dicarboxylate anion should have the ideal prerequisites to form a stable charge compensated polymeric chain structure as shown below.



This prediction has been realised and verified by the X-ray crystal structures of the terephthalate and fumarate salts of *trans*-bis(thiosemicarbazide)nickel(2+), $[Ni(tsc)_2]^{2+}[tere]^{2-}$ **1** [tsc = thiosemicarbazide, $H_2NC(S)NHNH_2$; tere = terephthalate, $C_6H_4(CO_2^-)_2$-1,4] and $[Ni(tsc)_2(OH_2)_2]^{2+}[fum]^{2-}$ **2** (fum = fumarate, *trans*-$O_2CCH{=}CHCO_2^-$), both of which exhibit infinite hydrogen-bonded arrays.

Red–green dichroic crystals of **1** and blue crystals of **2** suitable for single-crystal X-ray analyses were obtained by mixing aqueous solutions containing equimolar amounts of bis(thiosemicarbazide)nickel nitrate[18] and the disodium salt of the dicarboxylic acid. With the terephthalate, **1** is the sole product, whereas with disodium fumarate a small amount of green microcrystals, tentatively identified as $[Ni(tsc)_2]^{2+}[fum]^{2-}$, were produced alongside $[Ni(tsc)_2(OH_2)]^{2+}[fum]^{2-}$ **2**. Both **1** and **2** redissolve in Me_2SO at room temperature and in hot water.

The major difference in the crystal structures‡ of **1** and **2** involves the metal ion coordination geometry; **1** is square-planar (Fig. 1) whilst **2** is octahedral, with the additional axial coordination sites being occupied by aqua ligands (Fig. 2). In both complexes the tsc ligands are *trans*-coordinated. In **1**, the Ni–S and Ni–N bond lengths, 2.170(1) and 1.901(2) Å, and the N–Ni–S angle, 88.1(1)°, are similar to those in *trans*-$[Ni(tsc)_2(SO_4)]\cdot 3H_2O$[19] and *trans*-$[Ni(tsc)_2(SO_4)]$[18] but are slightly shorter than those in *trans*-$[Ni(tsc)_2][NO_3]_2$,[18] probably due to

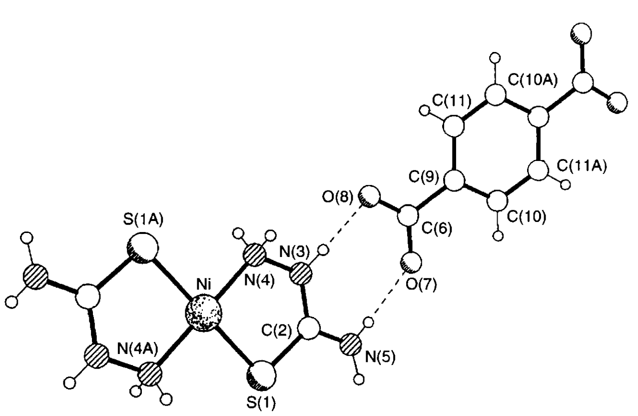


Fig. 1 The basic structural motif linking the cations and anions in **1**. The hydrogen bond distances (Å) and angles (°) are O(8)···H(3A) 1.86, O(8)···N(3) 2.70, N(3)–H(3A)···O(8) 177 and O(7)···H(5B) 2.01, O(7)···N(5) 2.77, N(5)–H(5B)···O(7) 177.

the longer-range axial Ni–O interactions in the nitrate complex. The Ni–S and Ni–N bond lengths in **2**, 2.401(1) and 2.093(2) Å, are, as expected, longer than those in **1** reflecting the higher coordination of the metal, and are similar to those observed in $[Ni(tsc)_2(OH_2)_2](NO_3)_2$,[18] although the Ni–O bonds in **2** are somewhat shorter, 2.064(2) *cf.* 2.123 Å.

Although the metal geometries of **1** and **2** differ, the crystal structures both show the same double hydrogen-bond interactons between the NH proton and one of the $C(S)NH_2$ protons of the cation and the two carboxylate oxygen atoms of the anion, which can be described in Etter's graph set notation[20] as $R^2_2(8)$. This leads in both cases to the anticipated extended polymeric chains of linked cations and anions, within which all of the N–H···O hydrogen bonds are strong (N···O distances in the range 2.70–2.83 Å) and have very similar geometries (N–H···O angles in the range 172–177°). These N···O distances are all shorter than the mean distance observed for hydrogen bonds between 1,1-diamino groups and carboxylate groups in the Cambridge Structural Database† emphasising the strength of the charge-augmented hydrogen bond interactions. The one-dimensional chains in both **1** and **2** are cross-linked by additional hydrogen bonding involving the second $C(S)NH_2$ proton and a carboxylate oxygen to form two-dimensional sheets, as shown in Fig. 3 for **1** and Fig. 4 for **2**. The inter-chain hydrogen-bond distances are somewhat longer than those within the chain with N···O distances of 2.95 Å in **1** and 2.92 Å in **2**. This cross-linking gives rise to the formation of 22- and 18-membered rings for **1** and two sets of 18-membered rings for **2**.

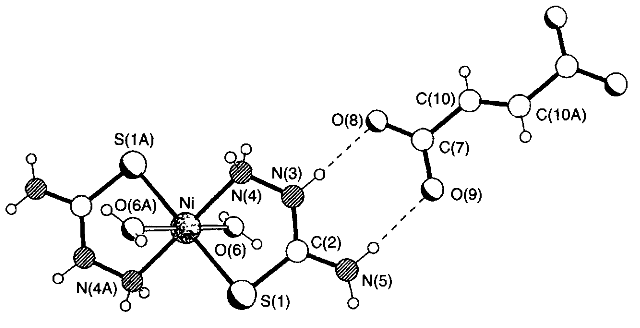


Fig. 2 The basic structural motif linking the cations and anions in **2**. The hydrogen bond distances (Å) and angles (°) are O(8)···H(3A) 1.94, O(8)···N(3) 2.79, N(3)–H(3A)···O(8) 172 and O(9)···H(5B) 2.01, O(9)···N(5) 2.83, N(5)–H(5B)···O(9) 174.

Although the main in-plane interactions in **1** and **2** are similar, the presence of the aqua ligands in **2** leads to differences in the inter-planar stacking interactions. In **1** these interactions involve N–H···O hydrogen bonds between the $NHNH_2$ hydrogen atoms which, unlike the other three hydrogens on the tsc ligand, are directed above and below the plane of the cation, and the terephthalate oxygen atoms. The alternating cation–anion–cation chains within each adjacently stacked sheet are not in register with each other and have the long axes of their terephthalate components inclined by *ca.* 65°. As a consequence of this, only one of the amino NH_2 hydrogen atoms is involved in inter-sheet hydrogen bonding (N···O 2.80, H···O 1.90 Å, N–H···O 167°). Within this stacked-sheet arrangement, the pseudo-axial positions of the nickel atoms are occupied by the π systems of the terephthalate anions, with Ni–π distances of 3.7 Å. The sheets of anions and cations are appreciably puckered, probably as a consequence of an unfavourable steric interaction between the terephthalate *o*-CH groups that would be present within a planar sheet geometry.

In **2** inter-sheet cross-linking is achieved *via* pairs of O–H···O hydrogen bonds (2.71 and 2.75 Å) between the axially coordinated aqua ligands within one sheet and oxygen atoms of pairs of fumarate anions from neighbouring chains in the next, and *vice versa*§ [graph set $R^2_4(8)$]. In contrast to the stacking arrangement in **1**, in which the cation–anion–cation chains in adjacent layers are angled with respect to one another, in **2** the chains are co-directional.

This research has clearly demonstrated that complementary double hydrogen bonds (DD=AA) can form the basis of a design concept leading to the formation of linear hydrogen-bonded metal-containing chains. Specifically, the interaction of thiosemicarbazide complexes and dicarboxylates with compensating charges can be utilised to create transition-metal containing hydrogen-bonded polymers. Furthermore, although the presence of the aqua ligands in **2** brings about a modification of the stacking arrangement within the crystal, the chain and sheet

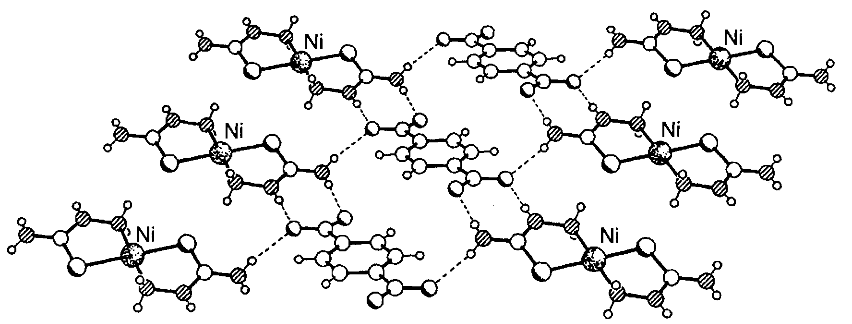


Fig. 3 The hydrogen-bonded tapes in **1** cross-linked into sheets. The inter-chain distances (Å) and angles (°) are O···N 2.95, O···H 2.10, N–H···O 165.

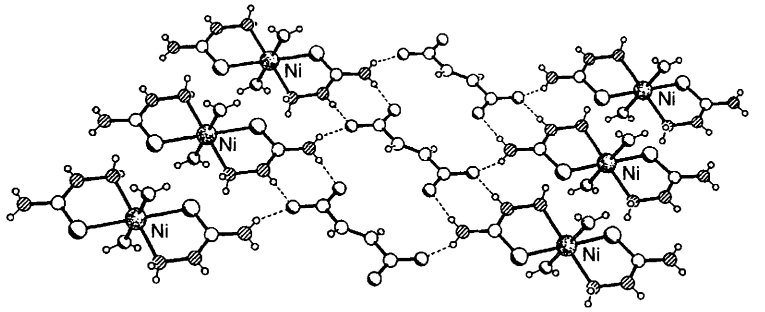


Fig. 4 The hydrogen-bonded tapes in **2** cross-linked into sheets. The inter-chain distances (Å) and angles (°) are O···N 2.92, O···H 2.17, N–H···O 155.

motifs are virtually unchanged from those in **1**. We are currently studying the effects upon these hydrogen-bonding networks of modification in the metal and the dicarboxylate anion and also investigating the magnetic properties of these new solid-state materials.

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Footnotes

† A search of the Cambridge Structural Database (Version 5.9) gave 67 complexes containing double hydrogen bonds between 1,1-diamino and carboxylate units, with a mean N···O distance of 2.84 Å.

‡ *Crystal data* for **1**: $C_{10}H_{14}N_6NiO_4S_2$, M = 405.1, red–green plates, crystal dimensions 0.50 × 0.27 × 0.07 mm, monoclinic, space group $P2_1/n$, a = 6.373(2), b = 16.769(5), c = 7.419(2) Å, β = 114.02(2)°, U = 724.2(4) Å^3, Z = 2 (the molecule has crystallographic C_i symmetry), D_c = 1.858 g cm^{-3}, μ(Cu-Kα) = 4.93 mm^{-1}, $F(000)$ = 416. 1143 independent data (2θ ≤ 124°) were collected on a Siemens P4/PC diffractometer using Cu-Kα radiation (λ = 1.54178 Å), graphite monochromator, ω-scans, and of these 1080 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. For **2**: $C_6H_{16}N_6NiO_6S_2$, M = 391.1, blue plates, crystal dimensions 0.90 × 0.40 × 0.08 mm, triclinic, space group $P\bar{1}$, a = 6.388(1), b = 7.702(2), c = 7.983(1) Å, α = 75.69(1), β = 79.16(1), γ = 79.26(1)°, U = 369.7(1) Å^3, Z = 1 (the molecule has crystallographic C_i symmetry), D_c = 1.757 g cm^{-3}, μ(Mo-Kα) = 1.63 mm^{-1}, $F(000)$ = 202. 1238 independent data (2θ ≤ 50°) were collected on a Siemens P4/PC diffractometer using Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, ω-scans, and of these 1219 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. Both structures were solved using direct methods and all non-hydrogen atoms were refined anisotropically by full-matrix least squares based on F^2 using absorption corrected data to give R_1 = 0.029(**1**), 0.023(**2**) and wR_2 = 0.082(**1**), 0.063(**2**) for the observed data and 127 (**1**), 125(**2**) parameters using the SHELXTL PC program system version 5. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The hydrogen bond distances (Å) and angles (°) are O(9A)···H(6A) 2.00, O(9A)···O(6) 2.75, O–H···O 168 and O(9B)···H(6B) 1.96 O(9B)···O(6) 2.71 and O–H···O 165.

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