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Novel Thiosalicylhydrazonates of Nickel(II)

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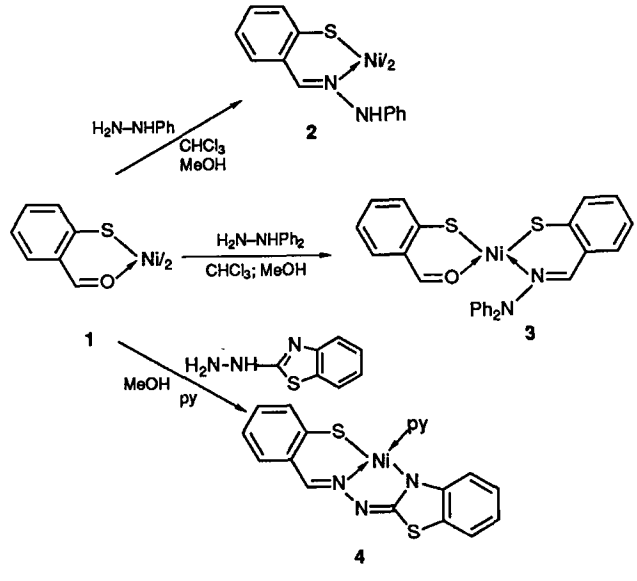
Template condensation of bis(thiosalicylaldehydato)nickel(II) **1** with a variety of mono- and di-*N*-substituted hydrazines results in novel hydrazonates of nickel with NiN_2S_2, NiN_2OS and NiN_3S coordination units; two such compounds (**3** and **4**) were characterized by X-ray crystallography.

Metal chelates derived from hydrazones of aromatic, heterocyclic and metalloorganic carbonyl compounds have been represented, in general, by complexes with N,O-donor environments.[1–3]

We have found that the interaction of thiosalicylaldehydatonickel(II) **1** with *N*-substituted hydrazines in chloroform or methanol results (see Scheme 1) in three complexes **2**–**4** which have been isolated and characterized by microanalysis and IR and ^{1}H NMR spectroscopies.† Compounds **2** and **3** have also been synthesized by direct interaction of the sodium salts of thiosalicylaldehyde, mono- or di-phenylhydrazine with nickel(II) acetate in ethanol.

All the species studied are diamagnetic; thus, the nickel ions have a near-planar coordination.

The molecular structures of compounds **3** and **4** were confirmed by X-ray crystal structure analysis (see Figs. 1 and 2).‡



Scheme 1

Chelate **3**, the first representative of a complex with two different hydrazonate ligands, has a *cis*-planar coordination of the central atom, which is a characteristic feature of NiN_2X_2 (X = S, Se) complexes[4] but is not known for $NiNOS_2$ compounds. The value of the dipole moment (4.65 D, benzene) and ^{1}H NMR data ($CDCl_3$) suggest that this compound has a *cis*-planar structure in solution too.

The nickel atom in **3** (see Fig. 1) has a near-planar coordination [the dihedral angle between the N(21)NiS(2) and O(1)NiS(1) planes is 11.9°] by one nitrogen, one oxygen and two sulphur atoms. The metallocycles in complex **3** have the form of an 'envelope' with the Ni atom positioned in the bent

† Spectroscopic properties and elemental analyses were found to be consistent with the proposed formulae.

‡ *Crystal data* for **3**: $[C_{26}H_{20}N_2OS_2Ni]$, $M_r = 499.3$, monoclinic, space group $C2/c$, $a = 20.893(6)$, $b = 12.226(1)$, $c = 21.449(6)$ Å, $\beta = 123.55(2)°$, $U = 4566(2)$ Å^3, $Z = 8$, $D_c = 1.45$ g cm^{-3}. Monochromatized Mo–Kα radiation, $\lambda = 0.7107$ Å, $\mu = 10.5$ cm^{-1}. Final R and R_w are 0.049 and 0.048 respectively, for 2564 reflections having $I \geq 2\sigma(I)$.

For **4**: $[C_{19}H_{13}N_4S_2Ni]$, $M_r = 420.1$, monoclinic, space group $C2/c$, $a = 17.288(3)$, $b = 10.561(1)$, $c = 19.8964(2)$ Å, $\beta = 95.93(1)°$, $U = 3607.3(9)$ Å^3, $Z = 8$, $D_c = 1.55$ g cm^{-3}. Monochromatized Mo–Kα radiation, $\lambda = 0.7107$ Å, $\mu = 13.1$ cm^{-1}. Final R and R_w are 0.040 and 0.035 respectively, for 2173 reflections with $I \geq 2\sigma(I)$.

Intensity data were collected at room temperature on a Syntex $P2_1$ diffractometer by the ω–2θ scan method. The structures were solved by the Patterson method (SHELXS) and refined by full-matrix least-squares techniques (SHELX). In both structures non-hydrogen atoms were placed in idealized positions and refined isotropically. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, *J. Chem. Soc., Chem. Commun.*

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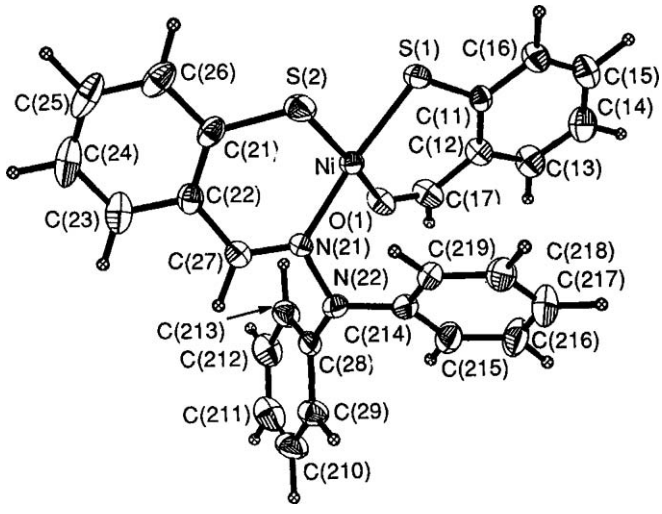

Fig. 1 Molecular structure of complex **3**. Selected bond lengths and valence angles: Ni—S(1) 2.149(2), Ni—S(2) 2.154(2), Ni—N(21) 1.931(5), Ni—O(1) 1.869(4) Å; S(1)NiS(2) 86.5(1), S(1)NiO(1) 95.5(1), S(2)NiN(21) 92.2(1), O(1)NiN(21) 87.1(2)°.

corner. The bend angle of ring 1 along the S(1)···O(1) line is 19.5° and the bend angle of the ring 2 along the S(2)···N(1) line is 39.4°. The atom N(22) of the NPh_2 substituent in **3** has an almost planar environment [the deviation of the N(22) atom from the plane defined by the three atoms bonded to it is 0.206(4) Å].

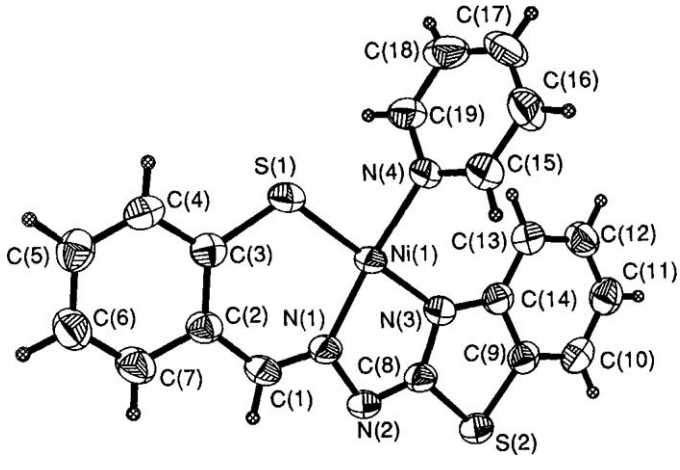

Fig. 2 Molecular structure of complex **4**. Selected bond lengths and valence angles: Ni—S(1) 2.137(1), Ni—N(1) 1.873(3), Ni—N(3) 1.915(3), Ni—N(4) 1.920(3) Å; S(1)NiN(1) 96.6(1), S(1)NiN(4) 84.8(1), N(1)NiN(3) 83.7(1), N(3)NiN(4) 95.5(1)°.

In complex **3** the S(1)···S(2) distance is 2.949(3) Å, which is much less than the double van der Waals radius of the sulphur atom (3.70 Å, see ref. 5).

In contrast with NiN_2O_2 complexes which prefer the *trans*-planar structure irrespective of the nature of the *N*-substituent, the NiN_2S_2 complexes prefer the *cis*-planar configuration.

We assume that the preservation of the carbonyl group in one of the two chelating ligands in the process of formation of complex **3** may be explained in terms of steric hindrance by the NPh_2-substituents in the *cis*-planar complex with two such groups.

The interaction of 2-benzthiazolylhydrazine with aldehydate **1** in the presence of pyridine in the reaction mixture yields a NiL·Py complex containing a ligand in the azine (azaalkane) tautomeric form which is unusual for uncoordinated heterocyclic hydrazones.[6]

In structure **4** (see Fig. 2) the dihedral angle between the S(1)NiN(1) and N(3)NiN(4) planes is 8.6°, thus the Ni atom has a near-planar N_3S coordination. Metallocycles NiN_3C and $NiSNC_3$ have almost planar configurations (± 0.034 and ± 0.019 Å respectively). The dihedral angle between the comparatively planar (± 0.003 Å) pyridine ring is 68.0°.

Thus we have first shown the possibility of obtaining metal hydrazonates with halcogenate atoms in the coordination sphere. It has been established that the type of and composition of nickel thiosalicylhydrazonates strongly depends on the size of the *N*-substituent.

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