Inorganica Chimica Acta, *166* (1989) 171–172

Preparation and Crystal Structure of Tetraethylammonium [Monochloro-bis(bis-μ-thiazoline-2-thionatonickelate(II))]. A Novel *S,N*-Thionate-bridged Binuclear Nickel Complex

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(Received July 6, 1989; revised September 14, 1989)

The chemistry of nickel with S-donor and S,N-donor ligands has received much attention in recent years, largely because the significance of nickel–sulfur bonds in nickel enzymes has been recognised [1].

Aryl thiolates, which have been widely used to simulate sulfhydryl–protein coordination, form distorted tetrahedral anions with divalent nickel, $[Ni(ArS)_4]^{2-}$ [2]. Although deprotonated heterocyclic thioamides have a propensity to form polymeric thionates [3], monomeric species are formed by benzthiazole-2-thionate (bztzt), $[Ni(bztzt)_2]$, with reputedly *cis*-square coordination about the metal [4]. In *fac*-$(Et_4N)[Ni(bztzt)_3]$ the metal is coordinated by three four-membered S,N-chelating ligands [5]. Pyrimidine-2-thionate and pyridine-2-thionate form similar complexes but in the *mer*-isomeric form [6].

Synthetic strategies are central to success in the case of heterocyclic thionate complexes of nickel(II). Aprotic solvents, complexed nickel(II), *in situ* ligand deprotonation and the correct order of addition of the reactants have generated mononuclear tris-chelates [5, 6]. With thiazoline-2-thione, however, we have obtained the novel product $((C_2H_5)_4N)[Ni_2(C_3H_2NS_2)_4Cl]$ (1) from the above synthetic strategy.

Experimental

Preparation of Compound 1

$(Et_4N)_2[NiCl_4]$ (1 mmol, 0.4610 g), prepared by a standard method [7], was dissolved in acetonitrile (10 ml). A suspension of thiazoline-2-thione (tztH) (3 mmol, 0.3510 g) in acetonitrile (10 ml), was added to the solution containing the tetrachloronickelate complex with continuous stirring. A solution of triethylamine (3 ml) in acetonitrile (10 ml) was then added to the reaction mixture which was then stirred for a further hour. An intense brown colouration resulted from the addition of triethylamine to the original reactants. The reaction mixture was left to stand overnight, which resulted in the production of brown crystals some of which were of diffraction quality. The product was recovered by filtration, washed with cold acetonitrile and dried *in vacuo*; yield 0.2294 g, (61.4%). *Anal.* Calc. for $C_{20}H_{28}N_5S_8ClNi_2$: C, 32.10; H, 3.74; N, 9.36; Ni, 15.8. Found: C, 32.18; H, 3.70; N, 9.37; Ni, 14.9%.

Crystal Structure Analysis

$((C_2H_5)_4N)[Ni_2(C_3H_2NS_2)_4Cl]$, $M = 747.8$, monoclinic space group $C2/c$; $a = 18.6671(8)$, $b = 12.0131(6)$, $c = 14.3848(6)$ Å; $\beta = 111.962(4)°$, $V = 2991.7$ Å^3; $D_m = 1.66(1)$, $D_c = 1.66$ g cm^{-3}, $Z = 4$, $\mu = 7.74$ mm^{-1}, $F(000) = 1536$. A total of 2358 independent reflections ($2\theta_{max} = 130°$) were measured on a Stoe–Siemens AED-2 diffractometer with Cu Kα ($\lambda = 1.54184$ Å) radiation. Of these reflections, 2128 were considered to be observed with $F_o > 4\sigma(F_o)$ ($\sigma_c(F)$ from counting statistics only). The non-H atoms were located by a combination of direct methods and difference synthesis [8] and refined by blocked-cascade, least-squares

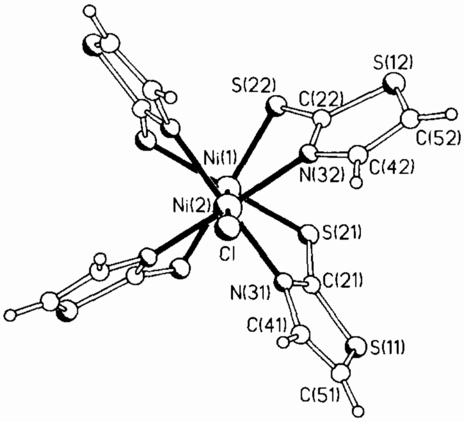

Fig. 1. Perspective view of the complex anion with the independent atoms labelled. Selected bond lengths (Å) and angles (°): Ni(1)–Ni(2), 2.648(2); Ni(1)–S(21), 2.217(1); Ni(1)–S(22), 2.233(2); Ni(2)–N(31), 2.086(5); Ni(2)–N(32), 2.068(4); Ni(2)–Cl, 2.381(2); Ni(2)–Ni(1)–S(21), 92.5(1); Ni(2)–Ni(1)–S(22), 90.8(1); S(21)–Ni(1)–S(22), 90.3(1); S(21)–Ni(1)–S(21a), 175.1(1); S(22)–Ni(1)–S(21a), 89.6(1); S(22)–Ni(1)–S(22a), 178.4(1); Ni(1)–Ni(2)–Cl, 180; Ni(1)–Ni(2)–N(31), 85.3(1); Ni(1)–Ni(2)–N(32), 85.6(1); N(31)–Ni(2)–N(32), 87.2(2); N(31)–Ni(2)–N(31a), 170.7(2); N(32)–Ni(2)–N(31a), 92.1(2); N(32)–Ni(2)–N(32a), 171.1(2). (The letter 'a' signifies an atom related by the symmetry operation: $-x, y, -z$.)

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0020-1693/89/$3.50

methods on F, to a minimum of $\Sigma w\Delta^2$ with anisotropic thermal parameters to a final $R = 0.0623$. Hydrogen atoms were included in the calculations for the anion; C–H = 0.96 Å, U(H) = 1.2 eqC. The cation is disordered over a centre of symmetry, consequently, no H atoms were included in the calculations for this ion (see also Supplementary Material). Selected bond lengths and bond angles of **1** are shown in Fig. 1.

Results and Discussion

Disappearance of the ν(NH) band (3200 cm^{-1}) coupled with the presence of ν(Ni–N) and ν(Ni–S) bands at 260/270 and 360/380 cm^{-1}, respectively, confirmed both deprotonation and S,N-coordination of the ligand (tztH). In the binuclear anion, the two independent nickel atoms as well as the chlorine atom occupy a crystallographic two-fold axis, consequently, only two of the four bridging ligands are independent. The anion has the classic eclipsed lantern configuration with the bridging ligands oriented so that the thionate S atoms are grouped around Ni(1) and the hetero N atoms are grouped around Ni(2). In addition, the chlorine atom is also coordinated to Ni(2). Consequently, Ni(1) has square-planar coordination and an S_4 donor set, and Ni(2) has square-based pyramidal coordination and a N_4Cl donor set. In neither case is the nickel atom significantly displaced from its planar environment. The average Ni–S distance is 2.225 Å, the average Ni–N distance is 2.077 Å and the Ni–Cl distance is 2.381 Å. The Ni–N distances are in the range reported for S,N-chelating heterocyclic thionates: 2.025(2)–2.087(2) Å, [5, 6]. In general, Ni–S distances vary significantly both in respect to the nature of the ligand and the metal environment; the values reported for **1**, however, are similar to those reported for a combination of bridging and terminal bonds in $[Ni_2(SC_2H_5)_6]^{2-}$ (2.201(2)–2.225(2) Å) which has distorted square Ni–S_4 coordination [9].

The combination of a relatively short Ni–Ni distance, 2.648(2) Å, and a room-temperature magnetic moment (μ_B) of 1.92 (per Ni atom) indicate the possibility of metal–metal bonding between the metal atoms in the binuclear anion. Alternatively, and more likely, the Ni(1) atom is diamagnetic, because of its square-planar NiS_4 coordination, and the paramagnetism ($\mu_B = 3.84$) is concentrated in the square-based pyramidal, NiN_4Cl, environment of the Ni(2) site. This interpretation eliminates the possibility of metal–metal interactions in the complex.

The solid-state, diffuse-reflectance spectrum of **1** consists of a broad band (200–1000 nm), which is mostly charge-transfer in character, but which also probably contains d–d bands from the Ni–S_4 moiety of the anion. A broad d–d band (1140–2000 nm, λ_{max} 1500 nm, 6.7×10^3 cm^{-1}) and a sharp d–d band (2280 nm, 4.4×10^3 cm^{-1}) probably originate from the square-based pyramidal environment at Ni(2) [10].

Comparisons with related structures are complicated by the fact that no thionate-bridged binuclear nickel complexes have been reported and thiolate-bridged binuclear nickel complexes tend to be diamagnetic [11].

Supplementary Material

Final bond lengths and angles, refined non-H atomic coordinates with anisotropic thermal parameters, H-atom coordinates with isotropic thermal parameters, and structure factor tables are available from the authors on request.

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