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$[\{\mathrm{Ni(3,2,3\text{-}tet)}(\mu\text{-}\mathrm{NCO})\}_n](\mathrm{ClO_4})_n$: structural characterization of the first monodimensional nickel(II)–cyanato system with a description of its ferromagnetic coupling

Albert Escuer*, Ramon Vicente, Joan Ribas and M. Salah El Fallah
Departament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028-Barcelona (Spain)

Xavier Solans and Mercé Font-Bardia
Departament de Cristal logrAfia i Mineralogia, Universitat de Barcelona, Martí Franqués s/n, 08028-Barcelona (Spain)

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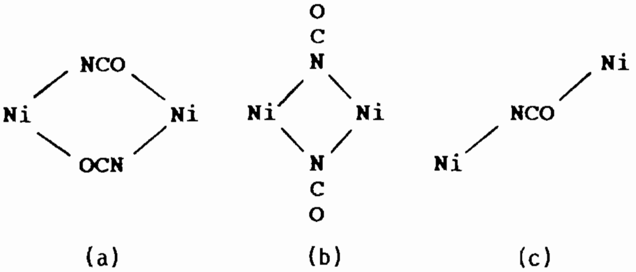
Abstract

The title compound has been characterized by means of X-ray crystallography. The cyanato ligand acts as a bridge between the square planar $[\mathrm{Ni(3,2,3\text{-}tet)}]^{2+}$ entities (3,2,3-tet = *N,N′*-bis(3-aminopropyl)-1,2-ethanediamine), giving an unprecedented chain structure. Crystal data for $[\{\mathrm{Ni(3,2,3\text{-}tet)}(\mu\text{-}\mathrm{NCO})\}_n](\mathrm{ClO_4})_n$: $FW = 374.47$, monoclinic, space group $P2_1/n$, $a = 10.587(2)$, $b = 12.395(2)$, $c = 11.871(2)$ Å, $\beta = 92.00(1)°$, $Z = 4$, $D_c = 1.597$ g cm^{-3}, $R = 0.038$, $R_w = 0.041$. The magnetic susceptibility data indicate weak ferromagnetic coupling

Key words: Crystal structures; Nickel complexes; Cyanate complexes; Magnetism

Introduction

Structurally characterized polynuclear nickel(II)–cyanato systems are scarce and the two reported to data are *cis* dinuclear systems with a double cyanato bridge [1, 2]. When the cyanato ligands are coordinated to two nickel atoms in an end-to-end fashion (a) the dinuclear compound presents weak antiferromagnetic (AF) coupling ($J = -4.4$ cm^{-1}) [1] and when the coordination is end-on (b) it presents weak ferromagnetic (FM) behavior ($J = +4.6$ cm^{-1}) [2]. The Hamiltonian used was $\mathscr{H} = -JS_1S_2$.



For other ions such as copper(II) [3], manganese(II) [4] or chromium(III) [5], polynuclear derivatives bridged only by the cyanato ligand, extremely low values of the $|J|$ parameter have been found (less than 1 cm^{-1} in all cases). From these experimental results, the cyanato bridge appears to be poorly effective as a superexchange pathway, but the correlation between the coordination mode and magnetic behavior (end-to-end ≡ AF, end-on ≡ FM), is similar to that reported for the most effective azido ligand.

A good strategy to avoid the synthesis of *cis* derivatives would be the use of tetraamines which preferentially give a *trans* arrangement around the nickel ion [6], with the aim of stabilizing the monobridged Ni–NCO–Ni (c) system. By using this strategy with the related azido ligand, we have recently reported the successful generation of the first monobridged 1D nickel(II)–azido systems [7].

Experimental

Synthesis of $[\{\mathrm{Ni(3,2,3\text{-}tet)}(\mu\text{-}\mathrm{NCO})\}_n](\mathrm{ClO_4})_n$

The complex $[\{\mathrm{Ni(3,2,3\text{-}tet)}(\mu\text{-}\mathrm{NCO})\}_n](\mathrm{ClO_4})_n$ was obtained by addition of an aqueous solution of sodium cyanate to an aqueous solution of equimolar amounts of nickel perchlorate hexahydrate and *N,N′*-bis(3-aminopropyl)-1,2-ethanediamine. Slow evaporation of this solution gives the title compound as well formed violet crystals. Satisfactory analytical results (C, H, N, Cl) were obtained.

Crystal data of $[\{\mathrm{Ni(3,2,3\text{-}tet)}(\mu\text{-}\mathrm{NCO})\}_n](\mathrm{ClO_4})_n$

$FW = 374.47$, monoclinic, space group $P2_1/n$, $a = 10.587(2)$, $b = 12.395(2)$, $c = 11.871(2)$ Å, $\beta = 92.00(1)°$, $Z = 4$, $D_c = 1.597$ g cm^{-3}, $F(000) = 784.0$, $R = 0.038$, $R_w = 0.041$ for 4033 reflections with $I \geqslant 2.5\sigma(I)$ collected on an Enraf-Nonius CAD4 diffractometer, $\theta/2\theta$ scan, $2 \leqslant 2\theta \leqslant 30°$. The structure was solved by Patterson synthesis, using the SHELXS [8] computer

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*Author to whom correspondence should be addressed

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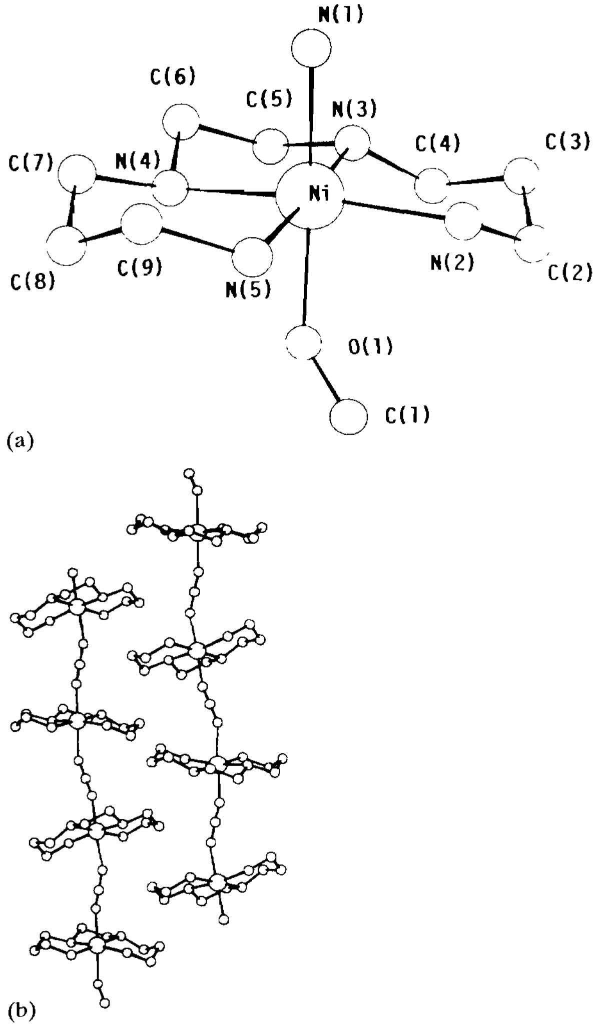

Fig. 1. A view showing the atom labelling (a) together with a perspective view of the arrangement of the chains in the *ac* plane (b) for $[\{Ni(3,2,3\text{-tet})(\mu\text{-NCO})\}_n](ClO_4)_n$. Main bond parameters: Ni–N(2) = 2.105(2), Ni–N(3) = 2.098(2), Ni–N(4) = 2.099(2), Ni–N(5) = 2.072(2), Ni–N(1) = 2.068(2), Ni–O(1) = 2.258(1) Å, Ni–N(1)–C(1) = 163.3(1), Ni–O(1)–C(1) = 132.0(1)°. The Ni–Ni′ distance is 6.284(1) Å, whereas the shorter Ni–Ni distance interchain is 7.665(1) Å.

program and refined by full-matrix least-squares method, with the SHELX76 [9] computer program.

Results and discussion

From a structural point of view this compound is the first monodimensional cyanato system reported to date. The structure consists of parallel 1D cyanato chains isolated by ClO_4^- anions found in the interchain space. No hydrogen bonds between the chains or perchlorate groups are present. The nickel(II) ion is placed in a distorted octahedral environment with the 323-tet ligand in *trans* arrangement, giving a practically planar $Ni–N_4$ fragment, Fig. 1. The two remaining *trans* coordination sites are occupied by two cyanato ligands that link the next $[Ni(3,2,3\text{-tet})]^{2+}$ fragments, giving the monodimensional system. The most significant bond parameters involve the nickel environment; the Ni–N distances are quite similar whereas the Ni–O(1) = 2.258(1) is larger as is often found. It is interesting to point out that the bond angles involving the cyanato ligand are greater than those found in double bridged dinuclear systems [1] (see caption of Fig. 1).

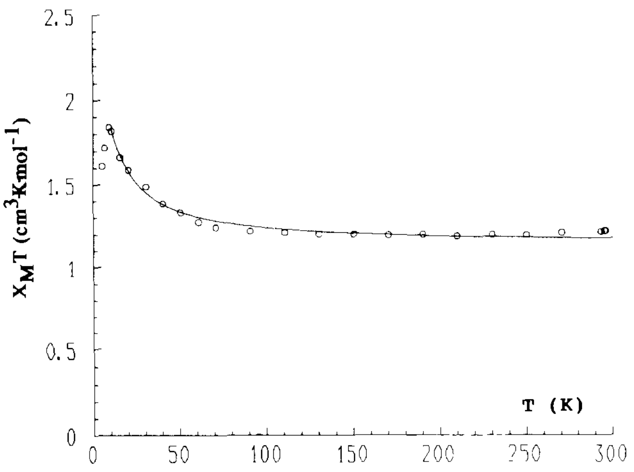

Fig. 2. Magnetic susceptibility plot of a polycrystalline sample of $[\{Ni(3,2,3\text{-tet})(\mu\text{-NCO})\}_n](ClO_4)_n$. The solid line shows the best fit obtained (see text).

The magnetic susceptibility measurements indicate a weak ferromagnetic coupling, Fig. 2, being the first case in which a Ni–OCN–Ni system shows this behavior. Experimental data have been fitted to the De Neef equation [10] up to 10 K, based on the spin Hamiltonian

$$\mathcal{H} = -2J\Sigma(S_iS_{i+1}) - D\Sigma(S_{iz}^2 - 2/3) + g\beta H\Sigma S_{iz}$$

and the superexchange parameters $J = +2.3$ cm^{-1}, $g = 2.14$ and $D = 3.9$ cm^{-1} have been obtained by minimizing the function $R = \Sigma(\chi_M^{calc} - \chi_M^{obs})^2/\Sigma(\chi_M^{obs})^2$ up to a value of 1.9×10^{-4}. This surprising result indicates that the generally accepted assumption that the ferromagnetic coupling is produced only by the end-on coordination of the cyanato ligand, supported in the spin-polarization effect [11], should be revised, giving special attention to the bond parameters found for this compound. Current efforts to synthesize related compounds as a basis for the theoretical explanation of the magnetic data are in progress.

Supplementary material

Tables of fractional atomic coordinates, thermal parameters, interatomic bond distances and angles are available on request from Dr A. Escuer.

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