Short Communication

Structure of a trinuclear nickel(II) complex bridged by 3,5-dimethylpyrazolate ($3,5\text{-Me}_2\text{pz}$), $[\text{Ni}_3(3,5\text{-Me}_2\text{pz})_4(\text{acac})_2]$

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Abstract

A novel trinuclear nickel(II) complex, $[\text{Ni}_3(3,5\text{-Me}_2\text{pz})_4(\text{acac})_2]$ ($3,5\text{-Me}_2\text{pz}$ = 3,5-dimethylpyrazolate, acac = acetylacetone), has been prepared and characterized crystallographically. The terminal and center nickel atoms are bridged by two $3,5\text{-Me}_2\text{pz}$, providing a trinuclear structure. The geometry of each nickel atom is square planar (SqPl) and these planes provide the zigzag mode. This is the first crystal structure of a trinuclear nickel(II) complex having a (SqPl)–(SqPl)–(SqPl) coordination arrangement. The Ni(1)···Ni(2) separation is 3.1972(5) Å and the Ni(II) complex has no attractive Ni(II)···Ni(II) interaction. The averaged Ni–N distance of $3,5\text{-Me}_2\text{pz}$ and Ni–O distance of acac are 1.876 and 1.850 Å, respectively.

Introduction

Many mono- and polynuclear nickel(II) complexes with N, O, P and S donor atoms have been prepared and their structures, magnetic and spectroscopic properties have been investigated [1]. In particular, it is expected that a trinuclear complex will produce an interesting geometry and magnetic property, which cannot be found in mono- and dinuclear complexes. A few trinuclear complexes with 1,2,4-triazole [2–6] and β-diketone [7] have been reported. In this study we have prepared a novel trinuclear nickel(II) complex using 3,5-dimethylpyrazolate and determined the structure by a single crystal structure analysis.

Experimental

Synthesis of $[\text{Ni}_3(3,5\text{-Me}_2\text{pz})_4(\text{acac})_2]$ *(1)*

$[\text{Ni}(\text{acac})_2]$ (acac = acetylacetone) (103.6 mg, 0.4 mmol) and sodium 3,5-dimethylpyrazolate ($3,5\text{-Me}_2\text{pzNa}$) (47.2 mg, 0.4 mmol) were mixed in THF (10 ml). A 0.7 ml hexane solution of triethylaluminum (*c.* 15%) was added to the yellow–green solution at −15 °C under ethylene atmosphere. The resultant orange suspension was filtered and the filtrate was sealed in a 5 mm diameter glass tube. The glass tube was allowed to stand for one month at −20 °C and orange crystals were collected. IR (KBr) 1578(ν(C=N)), 1526 (ν(C=C)) cm^{-1}. ^{1}H NMR (CDCl_3, 23 °C) 5.49(4H), 2.53(CH_3), 2.05(CH_3) ppm of Me_2pz and 5.23(CH_2), 1.77(CH_3) ppm of acac. Yield 20 mg (7%).

X-ray crystallography of **1**

An orange crystal of **1** was attached to the end of a glass fiber and mounted on a Rigaku AFC-5R automated diffractometer with graphite monochromated MoKα radiation ($\lambda = 0.71079$ Å). Intensity data were measured by ω–2θ scans at 23 °C and were corrected for Lorentz and polarization effects. Empirical absorption corrections were carried out. The structure was solved by a direct method (MITHRIL) [8] and refined by full-matrix least-squares calculations with anisotropic thermal parameters including isotropic hydrogen atoms located on difference Fourier synthesis. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography [9]. All calculations were performed using the TEXSAN crystallographic software package [10]. The final R and R_W values were 0.031 and 0.041, respectively.

Crystal data of 1 ($\text{Ni}_{1.5}\text{O}_4\text{N}_8\text{C}_{30}\text{H}_{42}$)

$FW = 377.41$, triclinic, space group $P\bar{1}$, $a = 9.782(1)$, $b = 12.602(2)$, $c = 7.5456(8)$ Å, $\alpha = 94.982(9)$, $\beta = 103.249(8)$, $\gamma = 71.608(8)°$, $V = 859.0(4)$ Å^3, $Z = 2$, $D_{\text{calc}} = 1.459$ g/cm^3, $F(000) = 394$, $\mu(\text{MoK}\alpha) = 16.80$ cm^{-1}, scan type ω–2θ, scan rate 8.0°/min, scan width $1.50 + 0.30 \tan\theta$, no. of reflections measured 4173 (total) and 3941 (unique), $F = 3\sigma(F_o)$ 3017, $R = 0.031$ and $R_W = 0.041$.

Results and discussion

The molecular structure of complex **1** is shown in Fig. 1, together with the atom labelling scheme. The

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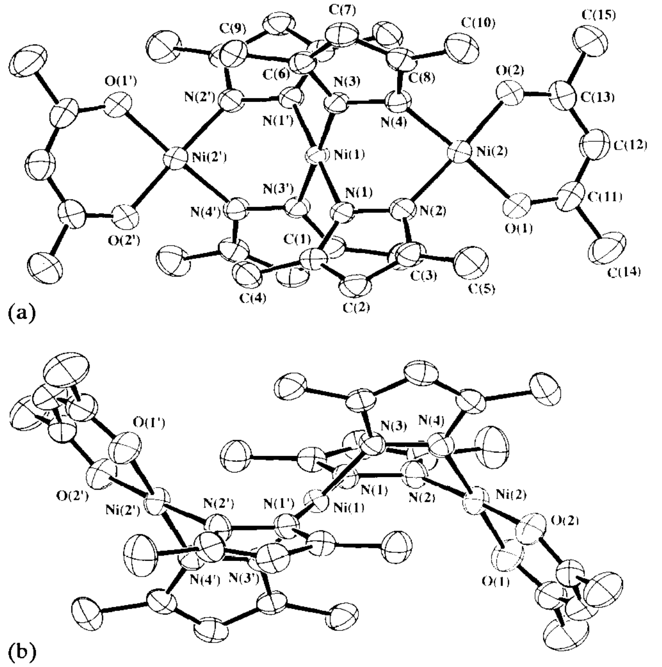

Fig. 1. Crystal structure of [Ni$_3$(3,5-Me$_2$pz)$_4$(acac)$_2$] (**1**) and the atom labelling scheme: (a) ORTEP view; (b) side view. Selected bond distances (Å) and angles (°) are as follows: Ni(1)···Ni(2), 3.1972(5); Ni(1)–N(1), 1.890(2); Ni(1)–N(3), 1.881(2); Ni(2)–O(1), 1.849(2); Ni(2)–O(2), 1.850(2); Ni(2)–N(2), 1.870(2); Ni(2)–N(4), 1.865(2); N(1)–Ni(1)–N(1'), 180.0; N(1)–Ni(1)–N(3), 89.08(9); N(1')–Ni(1)–N(3), 90.92(9); N(3)–Ni(1)–N(3'), 180.0; O(1)–Ni(2)–O(2), 94.40(9); O(1)–Ni(2)–N(2), 88.0(1); O(1)–Ni(2)–N(4), 176.62(9); O(2)–Ni(2)–N(2), 175.76(9); O(2)–Ni(2)–N(4), 88.92(9); N(2)–Ni(2)–N(4), 88.7(1).

selected bond distances and angles are listed in the caption. The complex has a centrosymmetric point on the Ni(1) atom. The terminal and center nickel atoms are bridged by nitrogen atoms of two 3,5-Me$_2$pz molecules. Furthermore, the terminal nickel atoms are coordinated to two oxygen atoms of acetylacetonate. The geometry of each nickel atom is square planar (SqPl) and these square planar planes provide the zigzag mode: the terminal planes are approximately perpendicular to the center plane. It is noted that three nickel atoms locate linearly. This is the first example of a trinuclear nickel(II) complex having a (SqPl)–(SqPl)–(SqPl) coordination arrangement which has been described crystallographically, although a few trinuclear nickel(II) complexes have been reported [2, 3, 7, 11].

The Ni(1)···Ni(2) separation of 3.1972(5) Å is significantly shorter than those (3.39(1)–3.801(1) Å) of analogous trinuclear nickel(II) complexes bridged by 1,2,4-triazole [2, 3]. However, this distance is much longer than those (2.443(1), 2.431(1) Å) of [Ni$_3$(bipyam-H)$_4$Cl$_2$] [11], indicative of an attractive direct Ni(II)···Ni(II) interaction. Complex **1** has probably no attractive Ni(II)···Ni(II) interaction.

The average Ni–N bridging distance of 1.876 Å is almost equal to that (*c.* 1.90 Å) reported for the mononuclear nickel(II) complexes [1] having a square planar geometry, and is shorter than those (2.05–2.352 Å) of the trinuclear complexes bridged by 1,2,4-triazole [2–6]. The average Ni–O distance of 1.850 Å is much shorter than those (1.997, 1.956 Å) of the trinuclear nickel(II) complex with acetylacetonate [7]. The averaged N–Ni–N angle of 90° is in the range (83.9–92.9°) of other complexes with 1,2,4-triazole [2, 3, 6].

Supplementary material

Tables of fractional atomic coordinates, thermal parameters, interatomic bond distances and angles are available on request from Professor M. Munakata.

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