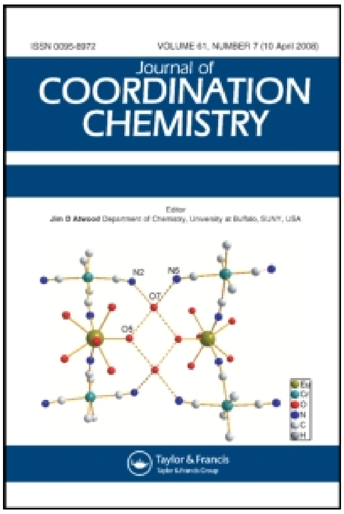

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CONTROL OF THE COORDINATION MODE OF NO_2^- BY THE NATURE OF THE AMINE LIGAND. CRYSTAL STRUCTURE OF THE NEUTRAL ZIGZAG POLYMERIC COMPOUND [mer-Ni(N-(2-Aminoethyl)-1,3-Propanediamine)-$(NO_2)_2$] (I)

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Note

CONTROL OF THE COORDINATION MODE OF NO_2^- BY THE NATURE OF THE AMINE LIGAND. CRYSTAL STRUCTURE OF THE NEUTRAL ZIGZAG POLYMERIC COMPOUND [*mer*-Ni(N-(2-aminoethyl)-1,3-propanediamine)-$(NO_2)_2$] (I)

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A polymeric zigzag complex, [*mer*-Ni(N-(2-aminoethyl)-1,3-propanediamine)$(NO_2)_2$] (I), containing a bridging μ-nitro(N,O), was obtained and its crystal structure was determined. Magnetic studies show the compound is antiferromagnetic. These results contrast to those for [Ni(3,3′-diamino-N-methyldipropylamine)$(NO_2)_2$] (II), which is a monomer.

Keywords: Nitrite; nickel; X-ray crystal structure; polymer

Because of its ability to function as an ambidentate ligand, the nitrite group has been of interest from the very earliest days of coordination chemistry.[1] Bridging ligands, μ-nitro(N,O)[2] and μ-nitro(O)[3] are very common. Moreover, it was observed recently that a nitrite group can also act as bridging ligand through μ-nitro(N,OO′)[4] and μ-nitro(O,O)[5] modes (Figure 1).

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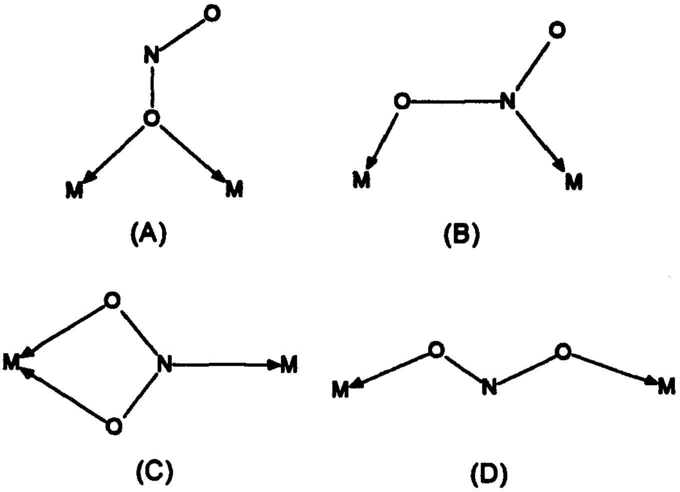

FIGURE 1 Modes of coordination of bridging NO_2^- ligands. (A) μ-nitro(N,O); (B) μ-nitro(O); (C) μ-nitro(N,OO′); (D) μ-nitro(O,O).

Compound (I)[†] was obtained from a deionized water solution of $NiCl_2$, amine and $NaNO_2$ in the ratio 1 : 1 : 3. Single crystals were obtained upon recrystallization and the systematic absences unambiguously determined the space group to be $P2_1/c$. The successful solution shows the compound to be a polymer, and there is only one nickel moiety within its asymmetric unit (Figure 2). Each nickel atom is in an octahedral coordination environment, and coordinated by three nitrogens of the amine ligand, one nitrogen of a nitro(N) group, one nitrogen of μ-nitro(N,O), and one oxygen of another μ-nitro(N,O) group. All the μ-nitro(N,O) groups in the compound are symmetry related. In the crystal structure, the μ-nitro(N,O) is disordered,[‡]

[†] Crystal data for compound I, $[Ni(N\text{-}(2\text{-aminoethyl})\text{-}1,3\text{-propanediamine})(NO_2)_2]$, $C_5H_{15}N_5O_4Ni$, monoclinic, space group $P2_1/c$, $a = 7.2849(6)$, $b = 22.740(3)$, $c = 6.7792(6)$ Å, $\beta = 111.370(8)°$, $V = 1045.8(4)$ Å^3. Cell dimensions were obtained from 25 reflections within 2θ range 10° and 22°. FW = 267.92 $Z = 4$ F(000) = 560, $D_{calc} = 1.702\,Mg \cdot m^{-3}$, $\mu = 1.867\,mm^{-1}$, Mo-Kα $\lambda = 0.71073$ Å. The intensity data were collected on an Enraf Nonius CAD4 diffractometer at 297 K, using the theta/2theta scan mode with maximum 2θ angle 33 degrees. Crystal size is 0.40 × 0.25 × 0.12. The h, k, l ranges used during structure solution and refinement are: h(min, max) -10, 0; k(min, max) 0, 34; l(min, max) -10, 11. A total of 4322 reflections were measured, of these 3948 are unique reflections, and 2670 reflections ($I > 2.5\sigma(I)$) were used for structure refinement. Merging R-value on intensities 0.016. Absorption corrections were made. The minimum and maximum transmission factors are 0.8360 and 0.9998. Unit weights were used. The final residuals are RF = 0.049, RwF = 0.039. The maximum shift/sigma ratio was 0.002. In the last D-map, the deepest hole was $-0.42\,e/Å^3$, and the highest peak $0.51\,e/Å^3$.

[‡] Population N_5, O_4: 0.66 and N_5' O_4': 0.34 (Figure 2).

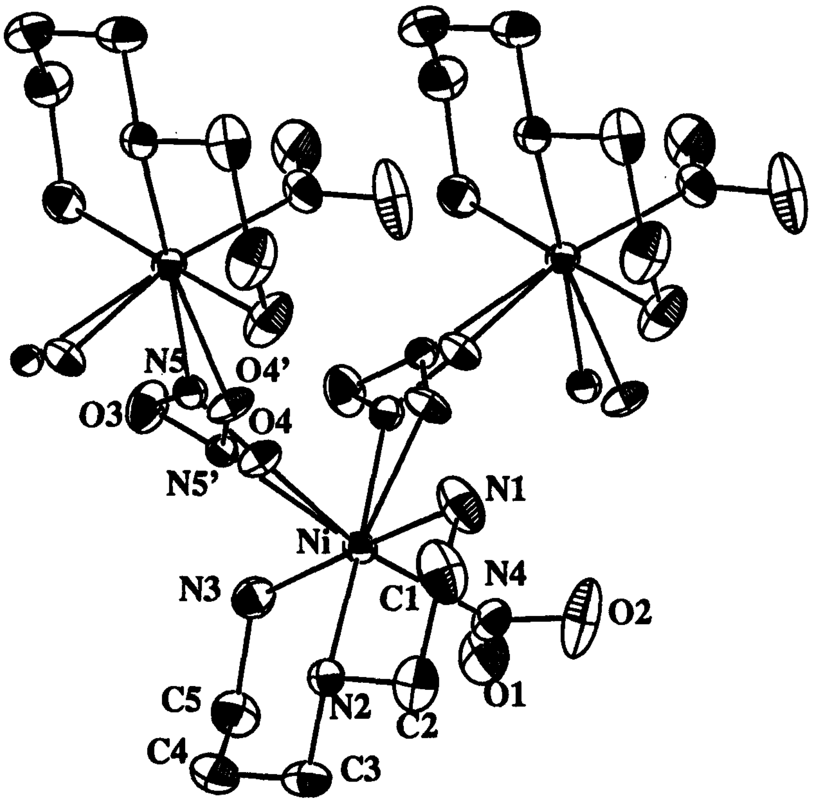

FIGURE 2 Crystal structure of polymeric compound [Ni(N-ethylamino-propane-1,2-diamine)$(NO_2)_2$] (I). Thermal ellipsoids are drawn at 30% probability level. Bond lengths: $Ni{-}N_1 = 2.060(3)$, $Ni{-}N_2 = 2.080(2)$, $Ni{-}N_3 = 2.052(2)$, $Ni{-}N_4 = 2.138(2)$, $Ni{-}N_5 = 2.158(3)$, $Ni{-}N'_5 = 2.203(3)$, $Ni{-}O_4 = 2.134(3)$, $Ni{-}O'_4 = 2.061(5)$, $N_4{-}O_1 = 1.224(3)$, $N_4{-}O_2 = 1.234$, $N_5{-}O_3 = 1.240$, $N_5{-}O_4 = 1.251(4)$, $N'_5{-}O_3 = 1.293(6)$, $N'_5{-}O'_4 = 1.263(7)$Å; Bond angles: $\angle O_1N_4O_2 = 115.9(3)$ $\angle O_3N_5O_4 = 114.7$ $\angle O_3N'_5O'_4 = 110.0°$

which is a fairly common occurrence in polymers linked by bridges of μ-nitro(N,O).[6] The packing diagram of compound (I) is shown in Figure 3.

Earlier we reported a similar synthesis using Medpt (Medpt = 3,3′-diamino-N-methyldipropylamine) replacing the N-(2-aminoethyl)-1,3-propanediamine. Compound (II), [Ni(Medpt)(NO_2)(O,O(N))]$_{1.5}$ was obtained and its crystal structure shows that there are two different molecules in the asymmetric unit with the same formula and very similar coordination environment.[7] Besides the coordinated amine ligand, each contains one monodentate nitro(N) and one bidentate chelating nitro(O,O). No polymer was formed. It has been suggested,[1] though it is not always true, that if steric

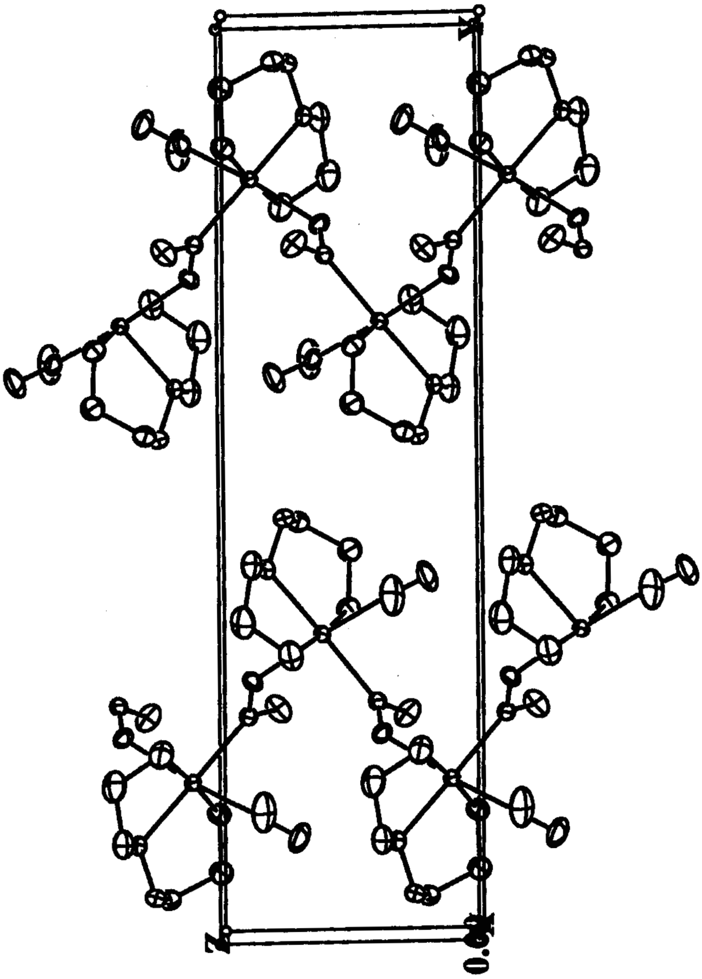

FIGURE 3 Packing diagram of polymeric compound [Ni(N-ethylamino-propane-1,2-diamine)$(NO_2)_2$] (I). Thermal ellipsoids are drawn at 30% probability level. Only the N_5, O_4 and their symmetry related atoms are shown for the disordered bridging NO_2 ligand.

factors are not important, the nitro ligand will prefer μ-nitro(N,O) to bidentate nitro(O,O); compound (**I**) showed this preference. As to compound (**II**), since the Medpt ligand provides much more steric crowding, the nitro group has to bind in the nitro(O,O) mode.[7]

The steric factor is very important to the nitro group coordination mode. Since compounds (**I**) and (**II**) were obtained from reaction of $NiCl_2$, amine ligand and $NaNO_2$ (1 : 1 : 1), we wonder whether forming a neutral complex

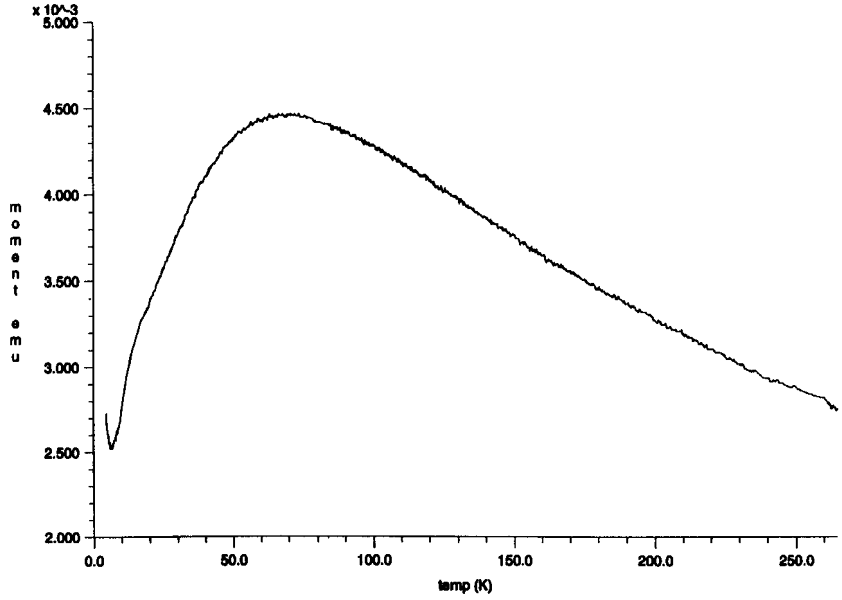

FIGURE 4 A typical χ *vs.* T curve for compound (**I**) (0.5 T cooling, 0.0455 g sample).

is also one of the factors that control binding modes of the NO_2^- ligand. This issue is currently under investigation.

The magnetic susceptibility measurements were carried out with an Oxford Vibrating Sample Magnetometer (installed 1996; equipped with a 1 T magnet) and in the cooling mode from 296 to 5 K. The results of the molar magnetic susceptibility, χ_m, plotted *vs.* temperature show the sample is antiferromagnetic with a maximum around 65 K (Figure 4).

Acknowledgements

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