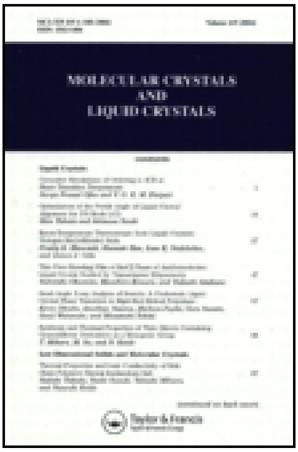

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Synthesis and Crystal Structures of Polymeric Nitridomanganese(V) and Nitridochromium(V) Complexes with a Tetradentate Schiff Base Ligand

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Novel polymeric nitridomanganese(V) and nitridochromium(V) complexes with a Schiff base ligand, [MnN(salpn)] and [CrN(salpn)] (H_2(salpn): *N,N'*-disalicylidene-1,3-propanediamine) were prepared by photolysis of azido complexes. X-ray crystal structure analyses show that the complexes have an isostructual polymeric structure (•••M≡N•••M≡N•••) with the N•••M distances being 2.528(3) Å for M=Mn, and 2.508(2) Å for M=Cr.

Keywords: nitridomanganese(V) complex; nitridochromium(V) complex; polymeric structure

INTRODUCTION

Recently, nitridomanganese(V) and nitridochromium(V) complexes with tetradentate Schiff base ligands such as [MnN(salen)] and [CrN(salen)] (H_2salen: *N,N'*-disalicylidene-1,2-ethanediamine) have been extensively studied as nitrogen atom transfer reagents in the fields of coordination chemistry and organic chemistry. All of the complexes reported have five-coordinate monomeric structures with square-pyramidal geometry. However, polymeric structures in the solid state are known for several complexes with a metal-oxo (M=O) or a metal-nitrido (M≡N) bond. For example, although most oxovanadium(IV) complexes with tetradentate Schiff base ligands like [VO(salen)] have five-coordinate monomeric structures, [VO(salpn)] (H_2salpn: *N,N'*-disalicylidene-1,3-propanediamine) with a six-membered N—N chelate ring moiety has a linear chain structure (•••V=O•••V=O•••) in the solid state [1]. For nitridometal complexes, polymeric linear chain structures (•••M≡N•••M≡N•••) are reported for V(V), Mo(VI), W(VI), Re(VII) complexes [2-6]. These results led us to prepare nitridomanganese(V) and nitridochromium(V) complexes with the salpn ligand in the hope of isolating the complexes in a polymeric form.

In this study, we report the preparation and crystal structures of novel polymeric nitridomanganese(V) and nitridochromium(V) complexes, [MnN(salpn)] and [CrN(salpn)] (FIGURE 1).

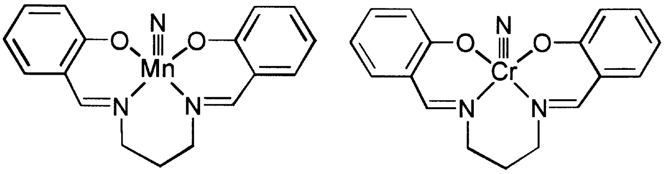

FIGURE 1 [MnN(salpn)] and [CrN(salpn)]

PREPARATION OF THE COMPLXES

The polymeric nitridomanganese(V) complex, [MnN(salpn)] was prepared by photolysis of the azidomanganese(III) complex, [MnN_3(salpn)] in acetonitrile [7]. In general, oxidation of manganese(III) complexes with NaClO or PhIO in the presence of NH_3 is also used in the preparation of the other Schiff base-nitridomanganese(V) complexes [8]. However, [MnN(salpn)] could not be prepared by oxidation of a manganese(III) complex in the presence of NH_3. Irradiation of [MnN_3(salpn)] with a high pressure mercury lamp in acetonitrile for two days gave [MnN(salpn)] in a 33 % yield. A brown complex in a polymeric form, [MnN(salpn)] was obtained by recrystallization of the product from acetonitrile or dichloromethane. A green complex in a monomeric form, [MnN(salpn)]•CH_3OH was obtained by recrystallization of the product from methanol. A polymeric nitridochromium(V) complex, [CrN(salpn)] was prepared by photolysis of the azidochromium(III) complex, $(CH_3)_2NH_2$[Cr$(N_3)_2$(salpn)] in acetonitrile for one day in a 54 % yield [9]. All the complexes are stable in air at ambient temperature.

The IR spectra of the polymeric and monomeric forms of [MnN(salpn)] show the Mn≡N stretching band at 1011 and 1043 cm^{-1}, respectively. The Mn≡N stretching frequency of the polymeric [MnN(salpn)] is a little shifted to lower energy than that of the monomeric one. The Cr≡N stretching bands of polymeric [CrN(salpn)] (956 and 961 cm^{-1}) are significantly shifted to lower energy than that of monomeric [CrN(salen)] (1012 cm^{-1}).

Nitrido complexes with a dimethyl-substituted salpn ligand, [MnN(Me_2salpn)] and [CrN(Me_2salpn)] (H_2Me_2salpn: *N,N'*-disalicylidene-2,2-dimethyl-1,3-propanediamine) were also prepared by photolysis of azido complexes. However, only monomeric forms were obtained for these complexes with an axially-oriented methyl group.

CRYSTAL STRUCTURES

X-ray crystal structure analyses of the polymeric and monomeric forms of [MnN(salpn)], and the polymeric form of [CrN(salpn)] were carried out. FIGURES 2 and 3 show ORTEP drawings of polymeric [MnN(salpn)] and monomeric [MnN(salpn)]•CH_3OH, respectively. Polymeric [MnN(salpn)] has a linear •••Mn≡N•••Mn≡N••• structure. The Mn≡N distance is 1.520(3) Å, and the Mn•••N distance is 2.528(3) Å. On the other hand, monomeric [MnN(salpn)]•CH_3OH has a five-coordinate square pyramidal structure with the Mn≡N distance being 1.513(3) Å.

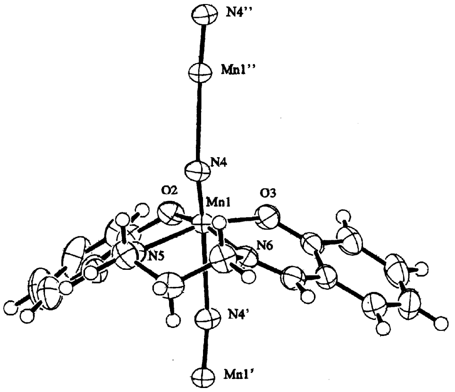

FIGURE 2 ORTEP drawing of polymeric [MnN(salpn)] [7].

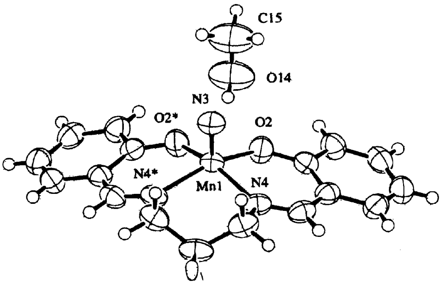

FIGURE 3 ORTEP drawing of monomeric [MnN(salpn)]•CH_3OH [7].

The crystal structure of polymeric [CrN(salpn)] is isostructural to that of polymeric [MnN(salpn)]. The space group ($P2_12_12_1$) is identical, and the unit cell parameters are related. The complex has a linear •••Cr≡N•••Cr≡N••• chain structure with the Cr≡N and Cr•••N distances being 1.559(2) Å and 2.508(2) Å, respectively. The Cr≡N units in [CrN(salpn)] are a little more strongly bonded to each other than the Mn≡N units in polymeric [MnN(salpn)]; the Cr•••N distance in [CrN(salpn)] (2.508(2) Å) is a little shorter than the Mn•••N distance in [MnN(salpn)] (2.528(3) Å). It is to be noted that the V=O units in polymeric [VO(salpn)] are more strongly bonded to each other than these complexes (the V•••O distance: 2.213(9) Å) [1].

MAGNETIC PROPERTIES

Nitridomanganese(V) and nitridochromium(V) complexes have a d^2 and a d^1 electron configuration, respectively. Polymeric [MnN(salpn)] with a $(d_{xy})^2$ electron configuration is diamagnetic [7]. Polymeric [CrN(salpn)] with a $(d_{xy})^1$ electron configuration shows a ferromagnetic interaction in a chain (J = + 8.4 cm^{-1}) [9]. A similar ferromagnetic intermolecular interaction is observed for polymeric [VO(salpn)] with the same $(d_{xy})^1$ electronic configuration [10]. However, the magnetic interaction in [CrN(salpn)] (J = + 8.4 cm^{-1}) is larger than that in [VO(salpn)] (J = + 5.2 cm^{-1}), while the distance between the Cr≡N units in [CrN(salpn)] is longer than that between the V=O units in [VO(salpn)].

SUMMARY

Novel polymeric [MnN(salpn)] and [CrN(salpn)] were prepared in this study. Formation of the polymeric structure for these complexes may be attributed to the weak coordination ability of the salpn ligand compared with the salen-type ligands, and crystal packing efficiency related to the conformation of the six-membered N—N chelate ring moiety [11].

References

[1.] M. Mathew, A. J. Carty, and G. J. Palenik, *J. Am. Chem. Soc.*, **92**, 3197 (1970).

[2.] W. Willing, R. Christophersen, U. Müller, and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **555**, 16 (1987).

[3.] S. C. Critchlow, M. E. Lerchen, R. C. Smith, and N. M. Doherty, *J. Am. Chem. Soc.*, **110**, 8071 (1988).

[4.] D. M. –T. Chan, M. H. Chisholm, K. Folting, J. C. Huffman, and N. S. Marchant, *Inorg. Chem*., **25**, 4170 (1986).

[5.] M. H. Chisholm, D. M. Hoffman, and J. C. Huffman, *Inorg. Chem.*, **22**, 2903 (1983).

[6.] W. Liese, K. Dehnicke, I. Walker, and J. Strähle, *Z. Naturforsch*, **34B**, 693 (1979).

[7.] M. Tsuchimoto, H. Iwamoto, M. Kojima, and S. Ohba, *Chem. Lett.*, **2000**, 1156 (2000).

[8.] J. D. Bois, J. Hong, E. M. Carreira, and M. W. Day, *J. Am. Chem. Soc*., **118**, 915 (1996).

[9.] M. Tsuchimoto, N. Yoshioka, and S. Ohba, *Eur. J. Inorg. Chem.*, in press.

[10.] M. Tsuchimoto and N. Yoshioka, *Chem. Phys. Lett.* **297**, 115 (1998).

[11.] M. Tsuchimoto, R. Kasahara, K. Nakajima, M. Kojima, and S. Ohba, *Polyhedron*, **18**, 3035 (1999).