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The Assembly and Molecular Structure of a Novel One-dimensional Cyanide-bridged $[Ni(pn)_2Ni(CN)_4]_n \cdot nH_2O$ Complex

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Abstract: The synthesis, structure and characterization of a new one-dimensional cyanide-bridged complex $[Ni(pn)_2Ni(CN)_4]_n \cdot nH_2O$ (where pn = 1,2-diaminopropane) are described. The structure of this complex consists of a one-dimensional polymeric chain $-Ni(pn)_2-NC-Ni(CN)_2-CN-Ni(pn)_2-$ in which the Ni(II) centers are linked by two CN groups.

Keywords: Cyanide bridged complex, polynuclear complex, crystal structure.

Introduction

Since the early work of Pedersen[1], Cram[2] and Lehn[3], molecular assembly has attracted much attention from scientists of different areas, ranging from chemistry to solid-state physics and biology, because of the potential impact on material science, catalysis and metallo-biochemistry[4]. The preparation and study of polynuclear, cyanide-bridged metal complexes have attracted considerable interest over the past decade[5-13]. Cyanide-bridged polynuclear complexes are suitable for the construction of such devices to obtain molecules capable of establishing specific functions especial for collection of electronic energy or electronic charge. The general synthetic approach for the metal assemblies is to utilize metal complexes having coordination ability as building blocks. We have done some work about cyanide-bridged complexes[7,9,10]. In the past years, $[Ni(CN)_4]^{2-}$ mainly was used in the crystal engineering of Hofmann-type and analogous structures that are built by the CN-linkages among square planar or tetrahedral tetracyanometallate(II) and octahedral metal(II) ligated with complementary ligand(s)[14]. Smekal and co-workers[15] reported the reaction of $[Ni(pn)_2]^{2+}$ and $[Ni(CN)_4]^{2-}$ and discussed their possible product. However, they couldn't determinate the structure of this kind of cyanide-bridged complex. Here we report the assembly, crystal structure and properties of $[Ni(pn)_2Ni(CN)_4]_n \cdot nH_2O$.

Experimental

The complex $[Ni(pn)_2Ni(CN)_4]_n{\cdot}nH_2O$ was prepared from 1,2-diaminopropane, nickel (II) chlorite and potassium tetracyanonickelate (II) in water. Since $K_2[Ni(CN)_4]$ has a tendency to decompose on heating and irradiation, the assembly of cyanide-bridged complex was performed at room temperature and crystallization was performed in a dark room. To a solution of $NiCl_2{\cdot}6H_2O$ (0.5mmol) and 1,2-diaminopropane (1mmol) was slowly added a solution of $K_2[Ni(CN)_4]{\cdot}2H_2O$ (0.25mmol). Upon standing for several days, the resulting purple single crystals were obtained for X-ray diffraction analysis‡. Yield: 83% Found: C, 30.59; H, 5.33; N, 29.28; Ni, 28.94%; Calcd. For $C_{10}H_{22}N_8Ni_2O$: C, 30.98; H, 5.72; N, 28.90; Ni, 30.28%.

Result and Discussion

In the present system, the formation of cyanide bridges in the 1-D complex was confirmed by the IR spectra in the region of the stretching vibrations of the cyanide ligands. The IR spectrum of the mononuclear compound $K_2[Ni(CN)_4]$ showed a band at 2121.94 cm^{-1} which can be assigned to CN stretching, whereas two strong absorption at 2127.90 and 2158.43 cm^{-1} have been observed for $[Ni(pn)_2Ni(CN)_4]_n{\cdot}nH_2O$, which probably arise from the bridging CN and terminal CN stretching vibrations, respectively. The bridging cyanide stretching vibration frequency is higher than ν_{CN} in $K_2[Ni(CN)_4]$, which may be explained by mechanical constraints on the CN motion imposed by the presence of the second metal center Ni(II) [16,17].

The electronic spectra of these complexes were measured in aqueous solution at room temperature. The electronic absorption of $[Ni(CN)_4]^{2-}$ displays MLCT with λ_{max} = 333 nm (ε = 345 $M^{-1}cm^{-1}$). The $[Ni(pn)_2]^{2+}$ shows a weak peak, λ_{max} = 558 nm (ε = 24 $M^{-1}cm^{-1}$), which is assigned to d-d transition. The UV-vis. spectra of $[Ni(pn)_2Ni(CN)_4]_n{\cdot}nH_2O$ shows a well-resolved maximum at λ_{max} = 308 nm (ε = 160 $M^{-1}cm^{-1}$) which is not obscured by absorptions of the mononuclear complexes. It is suggested that this high-energy band is assigned to MMCT transition from the octahedral Ni(II) ligated with 1,2-diaminopropane to the square planar tetracyano Ni(II). The one-electron optical CT transition process can be indicated by the following fomula:

$$\mathrm{Ni(II)\text{-}Ni(II)} \xrightarrow{h\nu} \mathrm{Ni(I)\text{-}Ni(III)}$$

An ORTEP drawing of an unit of complex 1 without water with the atom numbering scheme is shown in **Figure 1**. A view of the polymeric chain structure is given in **Figure 2**.

The structure of [Ni(pn)2Ni(CN)4]n shows that the asymmetric unit consists of one trans-[Ni(pn)2]2+ cation, one [Ni(CN)4]2- anion and one water molecule. Two cyano nitrogens (N(3) and N(3)') in trans mode coordinate to the adjacent Ni ions, through N(3) to Ni(1) of trans-[Ni(pn)2]2+ and through N(3)' to Ni(1)' of another trans-[Ni(pn)2]2+, to form a quasi wave form of the alternate array of the linear chain [Ni(pn)2Ni(CN)4]n as shown in Figure 2. The average bond angle 175.0(6)° of Ni(2)-C(4)-N(3) is near linearity, but the bond angle of Ni(1)-N(3)-C(4) is non-linear with an angle of 161.3(6)°. The bond angle 180° of N(1)-Ni(1)-N(1)*, N(3)-Ni(1)-N(3)*, C(5)-Ni(2)-C(5)', N(2)-Ni(1)-N(2)* and C(4)-Ni(2)-C(4)' is exactly linearity. The geometry of the ligand field of the Ni(1) ion is a six-coordination with tetragonal distorted-octahedral symmetry, the Ni(1)-N bond lengths ranging from 2.102(5) to 2.145(5) Å. The 1-D infinite chain structure is formed with the -Ni(1)-C-N-Ni(2)-N-C- linkages like a snake running and interlocking with its neighboring chain.

Figure 1. *ORTEP* stereoview of $[Ni(pn)_2Ni(CN)_4]$

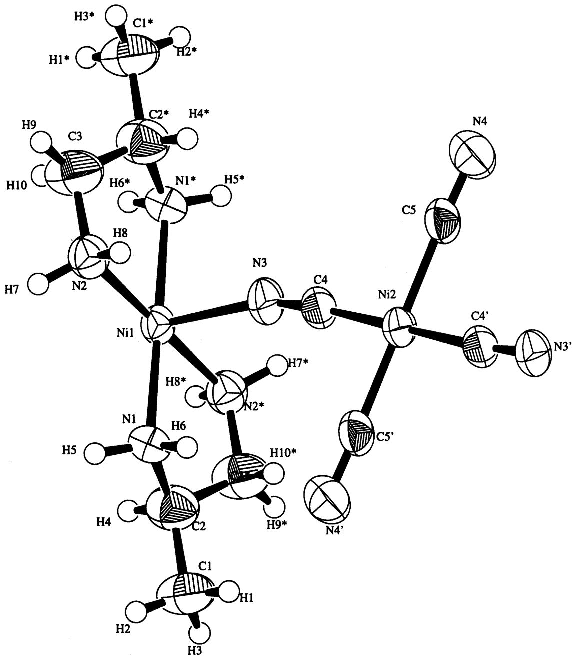
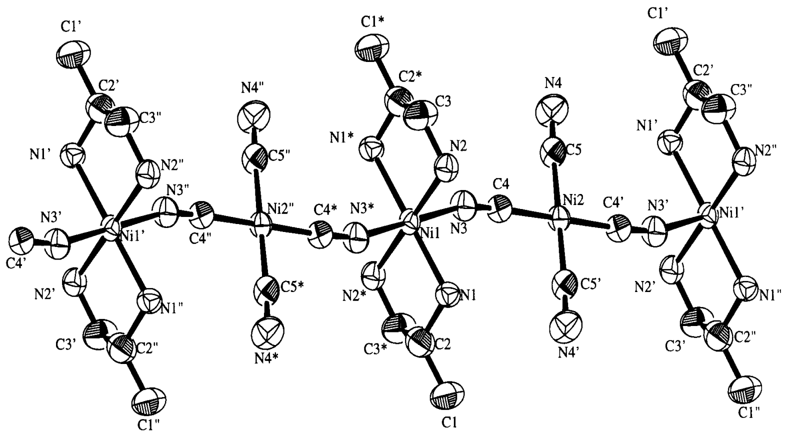


Figure 2. View of the CN-bridged polymeric $[Ni(pn)_2Ni(CN)_4]_n$ without H_2O



References and Notes

† Crystallographic parameters have been deposited in the editorial official of CCL.

‡ Crystal data: Formula $C_{10}H_{22}N_8Ni_2O$, monoclinic, Space Group C2/c(#15), a = 18.526(3), b = 7.882(2), c = 15.393(9) Å, β = 126.06(2)^o, V = 1817.1300 Å^3 , Z = 4, μ (MoKα) = 20.83 cm^{-1}, D_{calc} = 1.417 g/cm^3, M = 387.74, F_{000} = 808.00. The data were collected at a temperature of 15±1 °C to a maximum 2θ value of 55.0°. A total of 1704 reflections were collected. R = 0.066 and R_w = 0.092.

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