Two-dimensional Network Crown Ether Complex. Synthesis and Crystal Structure of 18-Crown-6 Complex: $[K(18\text{-}C\text{-}6)]_2[Cd(mnt)_2]$

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The novel complex $[K(18\text{-}C\text{-}6)]_2[Cd(mnt)_2]$ [18-C-6 = 18-crown-6, mnt = 1, 2-dicyanoethene-1, 2-dithiolate, $C_2S_2(CN)_2^{2-}$] was synthesized and characterized by elemental analysis, IR spectrum and X-ray diffraction analysis. The complex displays two-dimensional network structure of $[K(18\text{-}C\text{-}6)]$ complex segments and $[Cd(mnt)_2]$ complex segment bridged by S-K-S, S-K-N and N-K-N interactions between adjacent $[K(18\text{-}C\text{-}6)]$ and $[Cd(mnt)_2]$ units.

Keywords two-dimensional network, crown ether complex, 18-crown-6, crystal structure

Introduction

Recent years, coordination polymers have been received much attention because of their interesting physical properties such as electrical conductivity, magnetism, nonlinear optical properties and potential applications in separation and catalyst.[1] The modular approach using inorganic and organic building blocks has been successfully employed in preparing novel coordination polymers with interesting structures and properties. It has been reported that Cd complexes can form one-dimensional chain structure with crown ether. The reactions of 15-crown-5 with $CdCl_2$ and $CdBr_2$ afford the polymers: $[(CdCl_2)_2CdCl_2(15\text{-crown-}5)]_n$, $[(CdCl_2)_3CdCl_2(15\text{-crown-}5)]_n \cdot H_2O$ and $[(CdBr_2)_2CdBr_2(15\text{-crown-}5)]$ which consist of bridging halide interactions.[2-4] The complex cations of 12-crown-4 and 18-crown-6 can act as spacers/controllers to form the infinite zigzag chains with $[Cd(SCN)_3]^-$.[5,6] We have synthesized and characterized a series of one-dimensional chain crown ether-metal complexes $[K(18\text{-}C\text{-}6)]_2[ML_4](H_2O)$ (M = Pd, Pt; L = SCN, NO_2, I),[7,8] $[K(DB18\text{-}C\text{-}6)]_2[M(SCN)_4]$ (M = Pd, Pt)[9] and $\{[Na(18\text{-}C\text{-}6)][Na(18\text{-}C\text{-}6)(H_2O)]\}[Cu(mnt)_2]$.[10] In the present paper, the novel two-dimensional network complex: $[K(18\text{-}C\text{-}6)]_2[Cd(mnt)_2]$ was reported.

Experimental

Preparation

The title complex was prepared by adding $K_2[Cd(mnt)_2]$ (10 mL, 0.025 mol/dm^3) to 18-crown-6 (10 mL, 0.1 mol/dm^3) in 1,2-dichloroethane solution. The reaction mixture was stirred for 2 h at room temperature and then the organic phase was separated. The single crystal was obtained from diethyl ether/1,2-dichroloethane (4 : 1) solution, m. p. 253—254 ℃. FT-IR (KBr) ν: 2889(s), 2195(s), 1740(m), 1471(m), 1432(m), 1351(m), 1250(m), 1106(s), 960(s), 838(m), 514(m) cm^{-1}. Anal. calcd for $C_{64}H_{96}O_{24}N_8K_4S_8Cd_2$: C 38.45, H 4.90, N 5.60, S 12.81; found C 38.20, 4.57, N 5.46, S 12.64.

X-*ray crystallography*

A colorless crystal having approximate dimensions of 0.40 mm × 0.30 mm × 0.25 mm was mounted in a

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glass fiber. All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo K_α ($\lambda = 0.071073$ nm) radiation. The data were collected at temperature of 295(2) K to maximum θ value of 25.03°. The crystal structure belongs to triclinic, space group $P\bar{1}$ with cell dimensions: $a = 1.07317(18)$, $b = 1.3937(2)$, $c = 1.6834(3)$ nm, $\alpha = 108.128(3)$, $\beta = 99.895(3)$, $\gamma = 95.068(3)°$, $V = 2.3300(7)$ nm^3, $Z = 1$, $D_{calcd} = 1.425$ g/cm^3, $F(000) = 1028$. The structure was solved by direct method and expanded using Fourier techniques. The non-hydrogen atoms were refined by full-matrix least-squares calculations to $R_1 = 0.0404$ and $wR_2 = 0.0914$ for 9872 independent reflections [$R(\text{int}) = 0.0174$]. In the final difference map, the residuals are 4.68×10^2 e/nm^3 and -2.38×10^2 e/nm^3, respectively.

Results and discussion

The crystal structure and stereogram of the complex packing in a crystal unit cell are shown in Figs. 1 and 2. The complex consists of four [K(18-C-6)] complex segments and two [Cd(mnt)$_2$] complex segments. The Cd atoms do not bond directly to the O atoms of the crown ether and are coordinated by four S atoms from two mnt ligands instead and [Cd(mnt)$_2$] has a distorted tetrahedron configuration. The average bond lengths of Cd—S, S—C and C—N are 0.2524, 0.1732 and 0.1140 nm respectively. The average bond lengths of C—C and C=C are 0.1444 and 0.1358 nm respectively, which are consistent with the corresponding value in complex [$(C_6H_5)_4As]_2$[Zn(mnt)$_2$].[11] The dihedral angle of N(1)-C(49)-C(50)-C(51)-C(52)-N(2) and S(1)-C(50)-C(51)-S(2) is 2.9°, and other average dihedral angle of N-C-C-C-C-N and S-C-C-S is 6.0.

In the complex segment [K(18-C-6)], potassium atom lies within the crown ether ring. K—O bond lengths are at the range from 0.2689 nm to 0.2899 nm. K(2) atom of [K(18-C-6)] is also coordinated by S(4), S(5) atoms from mnt ligand of two [Cd(mnt)$_2$] complex segments respectively and the distances of K(2)—S(4), K(2)—S(5) are 0.3244(9), 0.3239(9) nm respectively, which are consistent with corresponding values in complex [K(18-C-6)]$_2$[UO_2(NCS)(H_2O)$_4$]

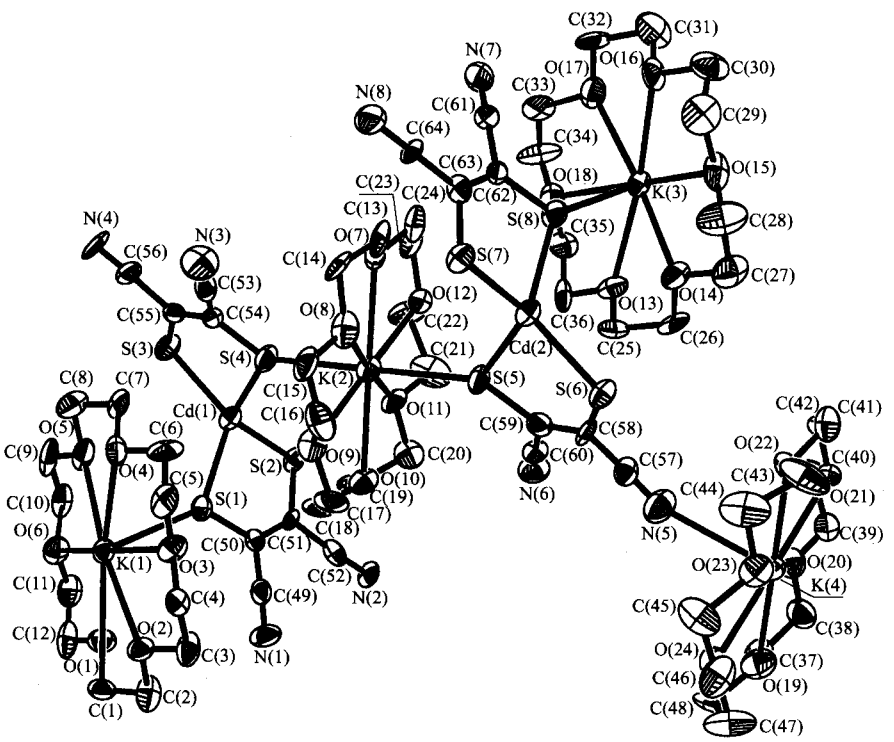

Fig. 1 ORTEP view of title complex.

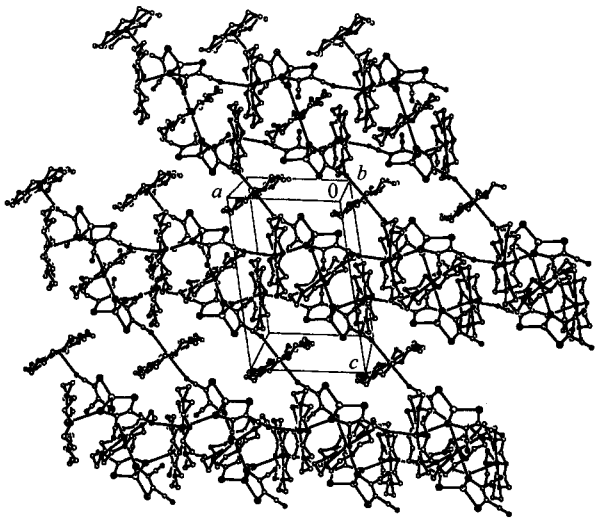

Fig. 2 Packing diagram of title complex.

[0.3179(1) nm].[12] The bond angle of S(4)-K(2)-S(5) is 179.4(3)°. K(1), K(3) atoms of [K(18-C-6)] segments are also coordinated by S(1), S(8) atoms from mnt ligands of two $[Cd(mnt)_2]$ complex segments respectively. The distances of K(1)—S(1), K(3)—S(8) are 0.3279(7), 0.3275(7) nm. The remainder of K(1), K(3) coordinating sphere are made up of N(2) #2 and N(8) #2 atoms from the other mnt ligands of the complex segments $[Cd(mnt)_2]$ at the distances of 0.2846(16) and 0.2898(14) nm respectively, which are consistent with corresponding values in complex $[K(18\text{-}C\text{-}6)]_2[Pd(SCN)_4]H_2O$[0.2847(6) nm].[13] Thus [K(18-C-6)] complex segments and $[Cd(mnt)_2]$ complex segments form an one-dimensional chain structure bridged by S-K-S and S-K-N interactions between adjacent [K(18-C-6)] and $[Cd(mnt)_2]$ units. Each one-dimensional chain is also connects with [K(18-C-6)] group to form two-dimensional network structure. The bond lengths of K(4)—N(5), K(4)—N(4) #3 are 0.297 and 0.2909(17) nm respectively and the bond angle of N(5)-K(4)-N(4) #3 is 176.6(8)°. To our knowledge, this is the first example which has two-dimensional network structure in mnt compound.

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