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Journal of Molecular Structure 738 (2005) 79–84

Journal of
MOLECULAR
STRUCTURE

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Two-dimensional structural topology involving Pt···K and K···S weak interactions: complex of *cis–anti–cis*-dicyclohexyl-18-crown-6 with K_2mnt and K_2PtCl_4

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Received 12 October 2004; revised 8 November 2004; accepted 11 November 2004
Available online 18 January 2005

Abstract

One inorganic–organic hybrid complex $[K(DC18C6\text{-}B)]_4[Pt(mnt)_2]_2$ (DC18C6-B = *cis–anti–cis*-dicyclohexyl-18-crown-6, isomer B; mnt = maleonitriledithiolate, 1,2-dicyanoethylene-1,2-dithiolate) was synthesized by the reaction of *cis–anti–cis*-dicyclohexyl-18-crown-6 with K_2mnt and K_2PtCl_4, and characterized by elementary analysis, ^{1}H NMR, FT-IR and UV–visible spectroscopy. The crystal structure was determined by X-ray single crystal diffraction. The complex crystallizes monoclinic, space group *P*2/*c* with crystallographic data: $a = 16.709(4)$ Å, $b = 10.201(2)$ Å, $c = 33.038(4)$ Å, $\beta = 90.143(2)$, $V = 5631.3(18)$ Å^3, $Z = 4$, $R_1 = 0.0679$, $wR_2 = 0.1280$. The complex shows a 2D network structure consisting of $[K(DC18C6\text{-}B)]^+$ complex cations and $[Pt(mnt)_2]^{2-}$ complex anions bridged by K–N coordinate bonds and Pt···K, K···S weak interactions.

Keywords: Dicyclohexyl-18-crown-6; Crystal structure; Platinum complex; Maleonitriledithiolate complex; Weak interactions

1. Introduction

The design, synthesis and characterization of coordination polymers have witnessed tremendous growth over the past decade [1,2]. Many polymeric networks have exhibited novel assembly modes and interesting electrical, magnetic, optical, zeolitic or catalytic properties [3–5]. One new class of inorganic–organic hybrid coordination polymers derived from crown ethers or their cations with transition metal bis(dithiolate) salts, in which the dithiolate ligands include mnt (1,2-dicyanoethylene-1,2-dithiolate) [6–10], i-mnt (1,1-dicyanoethylene-2,2-dithiolate) [11,12] and dmit (2-thioxo-1,3-dithiole-4,5-dithiolate) [13–19] (see Scheme 1), have become increasingly important due to their intriguing structural topologies and unique properties. In these crown ether polymers, coordinate bonds, hydrogen bonds and π–π stacking interactions usually act as the main driving forces of supramolecular architecture, whereas metal–metal interactions are infrequent. During the report of complex [K(18-cr-6)][$PtCl_3$(MeC≡CMe)] [20], the Pt–K distance of 4.03 Å was only mentioned by the way and not further discussed, perhaps, because the interaction made no important influence on the structure of complex. Cronin et al. [21] reported two sandwich-like salts, $[Rb(DC18C6\text{-}B)]_2[Ni(dmit)_2]$ and $[Cs(DC18C6\text{-}B)]_2[Ni(dmit)_2]$, and found short Rb···Ni and the shortest recorded Cs···Ni distance. Here, we report one new 2D structural complex, $[K(DC18C6\text{-}B)]_4[Pt(mnt)_2]_2$ (**1**), in which the main driving forces of supramolecular architecture are K–N coordinate bonds and Pt···K, K···S weak interactions.

2. Experimental

2.1. Materials and methods

K_2mnt was synthesized according to the literature [22]. All chemicals were commercially available and used without further purification.

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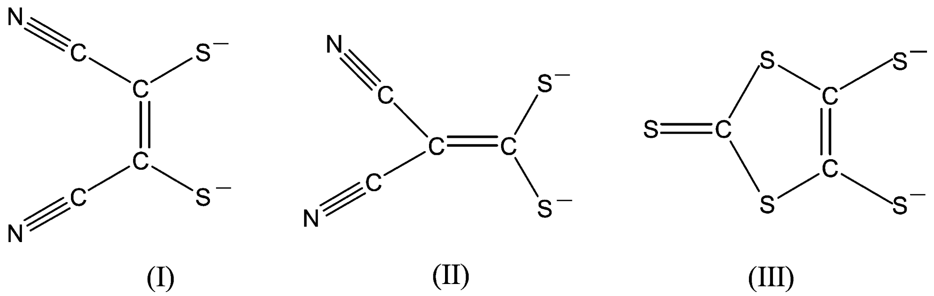
doi:10.1016/j.molstruc.2004.11.029


(I) (II) (III)

Scheme 1. The graphical formula for mnt (I), i-mnt (II) and dmit (III).

^{1}H NMR spectra were obtained on Varian Mercury Plus-400 spectrometer using TMS as internal reference and $CDCl_3$ as solvent. FT-IR spectra of the complex were measured on a Nicolet-460 FT-IR spectrometer in the range 4000–400 cm^{-1} as KBr pellets. UV–visible spectra were made on HP-8453 UV–visible spectrophotometer in acetone. The microanalytical data were obtained from a Perkin–Elmer 2400 II analyser. Thermogravimetric analysis was performed on a Perkin–Elmer Pyris I Thermogravimetric Analyzer with the heating rate of 10 °C/min from 50 to 750 °C. Nitrogen stream was used as an atmosphere. Cyclic voltammetric measurement at the exact potential scan rates (0.1 Vs^{-1}) was carried out on an EG&G PAR Model 273A at room temperature. Acetonitrile was used as the solvent, and $NaClO_4$ as supporting electrolyte (0.1 M). The measurement was performed on solution containing 0.001 M sample. Solution was deoxygenated by means of a steam of nitrogen for a few minutes. A platinum disc (3 mm diameter) was used as the working electrode. The counter electrode was a platinum plate and a saturated calomel electrode (SCE) was used as the reference electrode.

2.2. Synthesis

Complex **1** was prepared by adding 10 ml aqueous mixture of K_2PtCl_4 (0.1038 g, 0.25 mmol) and K_2mnt (0.2184 g, 1 mmol) to 10 ml dicyclohexyl-18-crown-6 (0.3722 g, 1 mmol) in 1,2-dichloroethane. The reaction mixture was stirred for about 3 h at room temperature. The organic phase was separated from the reaction solution. Crystals were obtained from 4:1 diethyl ether/1,2-dichloroethane solution over a period of 7 days. They were filtered, and washed with methanol followed by diethyl ether, and air-dried. Yield, 72% (based on Pt). Mp 205–206 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.288 (s, 4H, CH_2), 1.591 (s, 8H, CH_2), 1.901 (s, 4H, CH_2), 3.431 (s, 4H, CHO), 3.645–3.770 (m, 16H, CH_2O). The elemental analyses for $C_{48}H_{72}N_4K_2O_{12}PtS_4$, calcd: C, 44.39; H, 5.59; N 4.32. Found: C, 44.33; H, 5.46; N, 4.26. FT-IR (KBr): 2935 (s), 2858 (s), 2300 (w), 2195 (s), 1633 (m), 1473 (s), 1358 (m), 1306 (w), 1245 (m), 1151 (s), 1130 (s), 1091 (vs), 992 (s), 935 (m), 907 (w), 866 (w), 844 (w), 601 (m), 511 (m). UV–visible ($(CH_3)_2CO$, λ_{max}, nm): 340, 485.

2.3. X-ray crystallography

The X-ray diffraction experiment for complex **1** was made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at the temperature of 298(2) K. The structure was solved by direct method and expanded by using Fourier's technique and Shelxl-97 program. The non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. The hydrogen atoms were added theoretically, ridding on the concerned atoms and not refined. Crystallographic data for the complex are listed in Table 1.

3. Results and discussion

3.1. Synthesis

The crown ether–metal–maleonitriledithiolate complex was prepared possibly by the following reactions.

Table 1
Crystallographic data of complex **1**

Empirical formula	$C_{44}H_{72}N_4K_2O_{12}PtS_4$
Formula weight	1298.63
Crystal size (mm)	0.39×0.31×0.28
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	*P*2/*c*
a (Å)	16.709(4)
b (Å)	10.201(2)
c (Å)	33.038(4)
α (°)	90
β (°)	90.143(2)
γ (°)	90
V (Å^3)	5631.3(18)
Z	4
D (g cm^{-3})	1.532
F(000)	2656
Theta range (°)	2.42–25.06
Reflection collected	27801
Independent reflections	9576
Goodness-of-fit on F^2	1.007
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0679$, $wR_2 = 0.1280$
R indices (all data)	$R_1 = 0.1190$, $wR_2 = 0.1469$
Largest diff. peak and hole (e Å^{-3})	1.707, −1.296