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Cyano-bridged bimetallic complexes based on nitroprusside $[Fe(CN)_5(NO)]^{2-}$ and $[Cu(TAAB\text{-macrocycle})]^{2+}$: Synthesis, structure and thermal stability

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Abstract

Two new cyano-bridged bimetallic complexes, $[Cu(TAAB)Fe(CN)_5(NO)]\cdot 2H_2O$ (**1**) and $[Mn(bpy)_2(H_2O)Fe(CN)_5(NO)]\cdot H_2O$ (**2**) (where TAAB = tetrabenzo[*b*,*f*,*j*,*n*][1,5,9,13]tetraaza-cyclohexadecine and bpy = 2,2′-bipyridine), have been synthesized and characterized by elemental analyses, IR spectra and TG-DSC analyses. Single crystal X-ray structure analyses revealed that the complex **1** has a cyano-bridged binuclear structure in which Cu(II) center is coordinated by tetraazacyclic TAAB ligand to form an intriguing saddle-shaped structure, and Fe(II) center is in an octahedral coordination environment with nitrosyl group *trans* to the cyano-bridge. In complex **2**, Mn(II) center is *cis* six-coordinated and linked to nitroprusside though a bridging cyanide group to form a binuclear structure, while the nitrosyl group is *cis* to the cyano-bridge. The thermal stabilities of both complexes were investigated, which shows the nitrosyl and cyanide groups of nitroprusside released by two-steps in the temperature range of 200–380 °C.

Keywords: Nitroprusside; TAAB macrocycle; Bimetallic complex; Crystal structure; Thermal analysis

1. Introduction

Transition metal cyanides have been studied extensively over the past two decades due to their great importance in magnetism and other properties [1–3]. Recently, there has been a growing interest in the field of cyano-bridged bimetallic complexes based upon nitroprusside building block $[Fe(CN)_5(NO)]^{2-}$, which is of interest not only in connection with their various structural motifs but also in connection with their magneto-optical properties [4–6]. Planar macrocyclic complexes can accept one or two donor atoms at the axial positions to form cyano-bridged nitroprusside bimetallic compounds. A number of such bimetallic complexes have been assembled using nitroprusside and macrocyclic complexes as molecular building blocks [7–9].

In order to extend the study of macrocyclic complex and nitroprusside bimetallic complex, a tetraazacyclic TAAB ligand and its copper complex has been employed for the synthesis. Neutral TAAB ligand is Schiff-base tetramer of *o*-aminobenzaldehyde. Although it has been known for a long time, but its metal complexes are rare and none of them has binuclear or polynuclear structure until now [10–12]. We report here the synthesis of a cyano-bridged bimetallic complex $[Cu(TAAB)Fe(CN)_5(NO)]\cdot 2H_2O$ (**1**), and its crystal structure and thermal stability. Although the magneto-structural correlations for nitroprusside bimetallic complexes have been studied extensively, however, their thermal stability is still unknown. Furthermore, we prepared a new cyano-bridged bimetallic complex $[Mn(bpy)_2(H_2O)Fe(CN)_5(NO)]\cdot H_2O$ (**2**). Its structure and thermal stability is also reported here.

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2. Experimental

2.1. Materials and measurements

All chemicals and solvents used for synthesis were of reagent grade. $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ (Aldrich) was used as received. $(H_2TAAB)(BF_4)_2$ and its copper complex $[Cu(TAAB)](BF_4)_2$ were prepared according to the literature method [13,14]. Elemental analyses were performed on a Vario EL III elemental analyzer. Infrared spectra were recorded with a Nicolet A370 FT-IR spectrometer in KBr pellets in the 4000–400 cm^{-1} region. TG-DSC analyses were completed on a Netzsch STA 449C thermal analyzer at a heating rate of 10 °C min^{-1} in air.

2.2. Synthesis

$[Cu(TAAB)Fe(CN)_5(NO)]\cdot 2H_2O$ (**1**). A 5 ml methanol solution containing 0.02 mmol $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ was added to 10 ml methanol solution of 0.02 mmol $[Cu(TAAB)](BF_4)_2$ under stirring. The resulting red-brown solution was left undisturbed for three days in the dark. Dark red prismatic crystals of **1** were harvested in 33% yield based on Cu. Anal. Calcd. for $C_{33}H_{24}CuFeN_{10}O_3$: C, 54.44; H, 3.32; N, 19.24%. Found: C, 54.87; H, 3.30; N, 19.18%. IR (KBr, cm^{-1}): 3441 br, 2185 w, 2135 m, 1917 s, 1619 s, 1588 m, 1566 s, 784 m, 760 m.

$[Mn(bpy)_2(H_2O)Fe(CN)_5(NO)]\cdot H_2O$ (**2**). A 5 ml aqueous solution containing 0.1 mmol $Mn(ClO_4)_2\cdot 6H_2O$ was added to 5 ml methanol solution of 0.2 mmol 2,2′-bipyridine. To this mixture was added 10 ml methanol solution of 0.1 mmol $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ under stirring. The resulting red-brown solution was left undisturbed for one week in the dark. Red prismatic crystals were harvested in 53% yield based on Mn. Anal. Calcd. for $C_{25}H_{20}FeMnN_{10}O_3$: C, 48.48; H, 3.26; N, 22.62%. Found: C, 49.67; H, 3.09; N, 23.14%. IR (KBr, cm^{-1}): 3441 br, 2162 m, 2141 m, 1915 s, 1596 m, 1440 s, 1016 m, 769 m.

2.3. X-ray crystallography

The well-shaped single crystals of **1** and **2** were selected for X-ray diffraction study. Data collections of **1**, **2** were performed with graphite–monochromatic MoKα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart Apex-II CCD diffractometer at $T = 273(2)$ K. Determinations of the crystal system, orientation matrix and cell dimensions were performed according to the established procedures. Lorentz polarization and absorption correction were applied. The structures were solved by direct method with SHELXS-97 program and refined by full matrix least-squares on F^2 with SHELXL-97 program [15]. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated position. The crystal data and structure refinement results are summarized in Table 1.

Table 1
Crystal data and structure refinement for **1** and **2**

	Complex **1**	Complex **2**
Empirical formula	$C_{33}H_{24}CuFeN_{10}O_3$	$C_{25}H_{20}FeMnN_{10}O_3$
Formula weight	728.01	619.30
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a (Å)	13.3212(6)	14.8535(3)
b (Å)	14.8396(6)	14.0563(3)
c (Å)	16.7185(7)	13.1540(2)
β °	98.829(4)	97.688(1)
V (Å^3)	3265.8(2)	2721.67(9)
Z	4	4
D_{calc}(g cm^{-3})	1.481	1.511
Absorption coefficient (mm^{-1})	1.146	1.044
$F(000)$	1484	1260
Crystal size (mm^3)	$0.20\times0.12\times0.10$	$0.20\times0.10\times0.06$
Unique reflections	2870 [$R_{int} = 0.0721$]	4922 [$R_{int} = 0.0232$]
Data/restraints/parameters	2870/0/220	4922/0/371
$R[I > 2\sigma(I)]$	$R_1 = 0.0648$, $wR_2 = 0.1717$	$R_1 = 0.0260$, $wR_2 = 0.0657$
R (all data)	$R_1 = 0.0858$, $wR_2 = 0.1941$	$R_1 = 0.0322$, $wR_2 = 0.0683$
Goodness-of-fit on F^2	1.028	1.063

3. Results and discussion

3.1. Synthesis and IR spectra

The neutral cyano-bridged Cu(II)–Fe(II) binuclear complex **1** was obtained by reaction of $[Cu^{II}(TAAB\text{-macrocycle})]^{2+}$ cation with $[Fe(CN)_5(NO)]^{2-}$ anion in methanol solution, while Mn(II)–Fe(II) binuclear complex **2** was obtained by reaction of Mn^{2+} with 2,2′-bipyridine and $[Fe(CN)_5(NO)]^{2-}$ (1:2:1 molar ratio) in water–methanol solution. Since $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ is photochromic and tends to decompose upon heating or irradiation [4], the syntheses of **1** and **2** were performed at room temperature and crystallizations were carried out in the dark. The formulas of **1** and **2** have been confirmed by elemental analysis.

In general, IR absorption bands in the region of 1900–2200 cm^{-1} are due to the presence of CN^- and NO^+ stretching vibrations [16]. The absorption peak that appears at 2185 and 2162 cm^{-1} for **1** and **2**, respectively, is assigned to the ν(C≡N) stretching vibration of bridging cyanide group, while the band that appears at 2135 and 2141 cm^{-1} for **1** and **2**, respectively, is assigned to the ν(C≡N) stretching mode of four terminal cyanide groups. The band of ν(N=O) appears at 1917 and 1915 cm^{-1} for **1** and **2**, respectively, in accordance with the literature [17]. The benzene ring C=C vibration associated with TAAB ligand is found at 1619 cm^{-1}. The band at 1566 cm^{-1} is assigned to imine C=N stretching mode. The absence of characteristic strong absorption of BF_4^- and ClO_4^- indicates **1** and **2** are neutral complexes.