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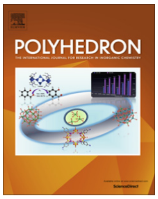

Syntheses, crystal structures and magnetic properties of two cyanide-bridged molecular squares $M_2^{II}–Co_2^{II}$ (M = Ru, Os) based on the diamagnetic cyanidometal $M(dppm)_2(CN)_2$

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ABSTRACT

Two tetra-nuclear cyanide-bridged molecular square complexes $[M^{II}(dppm)_2(CN)_2(Co^{II}Cl_2)]_2$ (M = Ru, **1**; M = Os, **2**) (dppm = bis(diphenylphosphino) methane) were synthesized and characterized by elemental analysis, IR, electronic absorption spectra and single-crystal X-ray diffraction analysis. Both the isostructure complexes **1** and **2** crystallize in monoclinic space group *P*21/*c*, and possess two *cis*-$M(dppm)_2(CN)_2$ (M = Ru, **1**; M = Os, **2**) and two $CoCl_2$ units through cyanido bridges. What's more, the environment around the Co(II) atoms in **1** and **2** define a slightly distorted tetrahedron, and are coordinated by two nitrogen atoms from the cyanide groups with *cis*-configuration and by two chlorine atoms. Temperature dependence of magnetic susceptibilities show both **1** and **2** are weak antiferromagnetic coupling between the paramagnetic Co(II) ions across a diamagnetic cyanidometal –NC–M(II)–CN– bridge. Furthermore, complex **1** exhibits spin-canted behavior. However, there is no such magnetic behavior in complex **2**, which may result from the more diffuse nature of the 5d orbitals with respect to 4d.

1. Introduction

Cyanide-bridged complexes have been obtained extensive attention due to their variable molecular structures and interesting magnetic coupling between paramagnetic metal centers through the cyanide bridge [1]. Until now, chemists have rationally designed and synthesized plenty of cyanide-bridged complexes with numerous topological structures, including zero dimensional (0D) molecular squares [2] or molecular clusters [3], 1D chains [4] and 2D [5] or 3D [6] networks, which showed fascinating magnetic behaviors. Among them, the combination of the anisotropy from Co(II) ions with other transition metal through cyanide-bridged have drawn our attention. And the corresponding cobalt complexes behaved much interesting properties, such as photoinduced magnetization [7], charge-transfer-induced spin transition [8], slow relaxation [9], single-molecule magnets(SMM) [10], single-chain magnets(SCM) [11], molecular magnetic nanowires, [12] and spin canting [13]. Interpretation of magnetic data for coordination complexes containing Co(II) centers is often difficult owing to the first order orbital contribution [10].

Recently, our group have synthesized a series of cyanido-bridged complexes with diamagnetic building blocks [14], some of which demonstrated strong coupling between paramagnetic metal through diamagnetic cyanidometal bridge [15]. Due to the magnetic nature, the exchange coupling between paramagnetic metals through diamagnetic metal decreases rapidly as the distance between paramagnetic metals increases. Thus by now the magnetic properties of polynuclear complexes with diamagnetic cyanidometal bridge [16] have seldom been investigated. In this work, we report the synthesis, characterization and magnetic properties of complexes $[M(dppm)_2(CN)_2(CoCl_2)]_2$ (M = Ru, **1**; M = Os, **2**) (dppm = bis(diphenylphosphino) methane), in which two paramagnetic Co(II) ions are bridged by diamagnetic cyanidemetals $M(dppm)_2(CN)_2$.

2. Experimental

2.1. Physical measurements

Elemental analyses (C, H, N) were carried out on a Vario MICRO elemental analyzer. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer using KBr pellets. UV–Vis absorption spectra were measured on a Perkin-Elmer

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Lambda 900 UV–Vis-NIR spectrophotometer. Temperature dependence of magnetic susceptibility was carried out using a Quantum Design Magnetic Property Measurement System (MPMS) SQUID-XL under an applied magnetic field of 1000 Oe in a 2–300 K temperature range and FC-ZFC (field-cooled and zero-field-cooled) measurement was carried out using MPMS under magnetic field of 50–1000 Oe in a 2–30 K temperature range. Diamagnetic corrections of complexes **1–2** were estimated from Pascal's Table. The diamagnetic susceptibilities are -1360.24×10^{-6} cm^3 mol^{-1} K for **1** and -1392.24×10^{-6} cm^3 mol^{-1} K for **2**.

2.2. Materials

All manipulations were performed under argon atmosphere with the use of standard Schlenk techniques unless otherwise stated. Dichloromethane was dried by distillation over calcium hydride and diethyl-ether was dried by distillation over sodium wire under argon atmosphere. Methanol was dried by distillation over magnesium under argon atmosphere. *cis*-Ru(dppm)$_2$(CN)$_2$, *cis*-Os(dppm)$_2$(CN)$_2$ were prepared according to the procedures in our other report [17]. All other reagents were available commercially and used without further purification.

2.3. *cis*-[Ru(dppm)$_2$(CN)$_2$(CoCl$_2$)]$_2$, **1**

Under argon atmosphere, a solution of CoCl$_2$·6H$_2$O (26.1 mg, 0.11 mmol) in MeOH (10 ml) was added into a solution of *cis*-Ru(dppm)$_2$(CN)$_2$ (92.1 mg, 0.10 mmol) in dichloromethane (10 ml) in a two-necked round-bottomed flask. After the mixture was stirred for 3 h at 35 °C, the solvent was removed and dichloromethane (20 ml) was added to the resultant solid. The mixture was filtered and the filtrate was concentrated under reduced pressure. The recrystallization of the resultant residue from a mixed solution of dichloromethane and ethyl-ether (1:3, 40 ml), gave **1** as light blue crystals 43.6 mg (41.4%). *Anal.* Calc. for $C_{104}H_{88}Cl_4Co_2N_4P_8Ru_2$: C, 59.38; H, 4.22; N, 2.66%. Found: C, 58.86; H, 4.87; N, 2.19%. IR (KBr, cm^{-1}): 2064 (CN), 2128 (CN). UV–Vis (CH$_3$CN), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 319(5300), 360(3200), 576(600), 672(1100).

2.4. *cis*-[Os(dppm)$_2$(CN)$_2$(CoCl$_2$)]$_2$·CH$_2$Cl$_2$, **2**·CH$_2$Cl$_2$

The procedure described for complex **2** was similar to complex **1** by using *cis*-Os(dppm)$_2$(CN)$_2$ (101.2 mg, 0.10 mmol) and CoCl$_2$ ·6H$_2$O (26.1 mg, 0.11 mmol). The product was obtained as blue crystals. Yield: 45.3 mg (36.3%). *Anal.* Calc. for $C_{104}H_{88}Cl_4Co_2N_4P_8Os_2$: C, 54.75; H, 3.89; N, 2.46%. Found: C, 54.79; H, 3.96; N, 1.78%. IR (KBr, cm^{-1}): 2066 (CN), 2130 (CN). UV–Vis (CH$_3$CN), λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1}): 322(6100), 368(300), 573(470), 672(890).

2.5. X-ray structure determination

The single crystal data of complexes **1** and **2** were collected on Saturn724+ CCD diffractometers equipped with graphite-monochromatic Mo K$_\alpha$ (λ = 0.71073 Å) radiation using an ω scan mode at 123 K. The structures were solved by direct methods and refined by full-matrix least-squares method on F^2 with anisotropic thermal parameters for non-hydrogen atoms using the *SHELXL-97* program suite [18]. Hydrogen atoms were calculated at idealized position and were refined using a riding model on their respective atoms. The *R* values are defined as $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $\omega R_2 = [\Sigma[\omega(F_o^2-F_c^2)^2]/\Sigma[\omega\ (F_o^2)^2]]^{1/2}$. The detail of crystal data were summarized in Table 1, and selected bond lengths and angles for complexes **1–2** were presented in Table 2.

3. Results and discussion

3.1. Syntheses

Complexes **1** and **2** were prepared in a straightforward way by reaction of *cis*-M(dppm)$_2$(CN)$_2$ (M = Ru, Os) in dichloromethane solution with equivalent molar CoCl$_2$·6H$_2$O in CH$_3$OH solution under ambient conditions. By slow diffusion of diethyl-ether into the dichloromethane solution, the blue crystals of **1** and **2** suitable for X-ray diffraction have been obtained. Both the complexes were characterized by IR, electronic absorption spectra, elemental analysis and single-crystal X-ray diffraction analysis.

The ν_{CN} of cyanide-bridged complexes are 2064 and 2128 cm^{-1} for **1**, 2066 and 2130 cm^{-1} for **2**, respectively, which are the combination of symmetric and asymmetric stretching frequencies. The separation between the two ν_{CN} bands of the cyanide-bridged complexes (**1–2**) larger than those of related cyanide precursors (2069 and 2076 cm^{-1} for *cis*-Ru(dppm)$_2$(CN)$_2$, 2088 and 2108 cm^{-1} for *cis*-Os(dppm)$_2$(CN)$_2$).

3.2. Crystal structures

The structural drawings of **1** and **2** are shown in Fig. 1. Both complexes **1** and **2** crystallize in monoclinic space group *P*21/*c*. In **1** and **2**, two *cis*-M(dppm)$_2$(CN)$_2$ (M = Ru, **1**; M = Os, **2**) units bridge two CoCl$_2$ through the cyanido bridges in a *cis*-position to form [2+2]-type discrete molecular square. In addition, complex **2** has a CH$_2$Cl$_2$ solvent molecule, while complex **1** has no solvent molecules. It has been reported that tetracoordinate Co(II) complexes often exhibit a distortion from the ideal T_d into D_{2d}, C_{2v} or C_1 [19]. Herein, the Co(II) atom in **1** and **2** is coordinated by two nitrogen atoms from the cyanide groups and by two chlorine atoms, forming a slightly distorted tetrahedron with nearly C_{2v} symmetry. Both the Ru(II) and Os(II) atoms define a

Table 1
Crystal data and structural refinement parameters for complexes **1–2**.

	1	2
Chemical formula	$C_{104}H_{88}Cl_4Co_2N_4P_8Ru_2$	$C_{105}H_{90}Cl_6Co_2N_4Os_2P_8$
Formula weight	2103.34	2366.53
Colour and habit	blue prism	blue prism
Crystal size(mm)	0.622 × 0.321 × 0.100	0.214 × 0.088 × 0.041
T (K)	123	123
Crystal system	monoclinic	monoclinic
Space group	*P*21/*c*	*P*21/*c*
a (Å)	24.407(12)	24.402(11)
b (Å)	15.540(7)	15.493(6)
c (Å)	27.312(13)	27.186(12)
α (deg)	90.00	90.00
β (deg)	100.184(14)	100.717(10)
γ (deg)	90.00	90.00
V (Å^3)	10196(8)	10099(8)
Z	4	4
ρ_{calcd} (g/cm^3)	1.370	1.556
λ (Mo Kα, Å)	0.71073	0.71073
μ(Mo K$_\alpha$, mm^{-1})	0.887	3.165
Completeness	99.7%	99.6%
F(000)	4280	4704
h, *k*, *l*, range	$-29 \leqslant h \leqslant 29$, $-18 \leqslant k \leqslant 18$, $-32 \leqslant l \leqslant 32$	$-29 \leqslant h \leqslant 29$, $-18 \leqslant k \leqslant 18$, $-32 \leqslant l \leqslant 31$
θ range(deg)	2.14–25.00	2.01–25.00
Reflections measured	17908	17717
R_{int}	0.0809	0.0802
Params/restraints/ data(obs.)	1105/78/13333	1144/99/13204
GOF	1.125	1.166
R_1, $_\omega R_2$($I > 2\sigma(I)$)	0.0858, 0.2215	0.0953, 0.2270
$R1$, $_\omega R_2$ (all data)	0.1112, 0.2504	0.1226, 0.2586