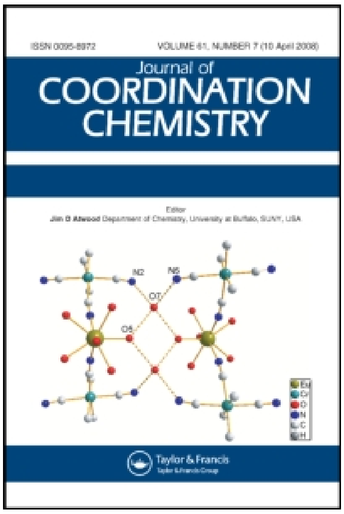

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

$[Cu_3(dppm)_3(\mu_3\text{-}I)_2][(0.5TCNQ)]$, a radical salt derived from a donor with a copper(I) trimer

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To cite this Article Song, Yong-Qin , Ma, De-Yun , Zhan, Shu-Zhong , Su, Jia-Yin and Xu, Jian-Wen(2008) '$[Cu_3(dppm)_3(\mu_3\text{-}I)_2][(0.5TCNQ)]$, a radical salt derived from a donor with a copper(I) trimer', Journal of Coordination Chemistry, 61: 24, 4004 — 4010

To link to this Article: DOI: 10.1080/00958970802195426

URL: http://dx.doi.org/10.1080/00958970802195426

Journal of Coordination Chemistry
Vol. 61, No. 24, 20 December 2008, 4004–4010

$[Cu_3(dppm)_3(\mu_3\text{-}I)_2][(0.5TCNQ)]$, a radical salt derived from a donor with a copper(I) trimer

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(*Received 25 January 2008; in final form 5 March 2008*)

A radical salt **1**, $[Cu_3(dppm)_3(\mu_3\text{-}I)_2][(0.5TCNQ)]$, has been prepared by reaction of CuI, dppm (diphenylphosphinomethane) and TCNQ (7,7′,8,8′-tetracyanoquinodimethane) with a molar ratio of 1 : 1 : 0.5 and characterized by IR, UV–Vis and solid-emission spectroscopy. Its structure was determined by X-ray crystallography. **1** also has photoluminescence ($\lambda_{max} = 653$ nm) at room temperature. Magnetic properties indicate that TCNQ is in the reduced state ($TCNQ^{2-}$).

Keywords: Copper cluster; Charge transfer; Crystal structure; Luminescence

1. Introduction

TCNQ is electron poor and forms numerous donor-acceptor compounds [1], where the radical anions are stabilized by charge and spin delocalization, forming numerous stable electron transfer salts. Typically, these easily reducible compounds form radical ions $HTCNQ^{\bullet -}$ or even dianions $TCNQ^{2-}$ [2, 3] in their reactions with metal complexes. Compounds containing TCNQ have attracted attention due to their interesting optical and magnetic properties in addition to playing the most important role in discovery and development of molecule-based materials exhibiting metal-like electrical conductivity [4], superconductivity [5] and ferromagnetic ordering [6].

Our interests focus on the synthesis of new inorganic/organic charge-transfer solids comprised of multinuclear transition-metal complexes and organic donors or acceptors. Herein, we report the assembly of a new radical salt **1**, $[Cu_3(dppm)_3(\mu_3\text{-}I)_2][(0.5TCNQ)]$, and structural, magnetic and spectroscopic characterization.

2. Experimental

CuI, dppm, and TCNQ were purchased from commercial sources and used as received.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970802195426

2.1. *Physical measurements*

Infrared spectra were recorded (4000–400 cm^{-1}) as KBr disks on a Bruker 1600 FTIR spectrometer. Electronic spectra were recorded on a Hitachi U-3010 (UV–Vis) spectrophotometer in water. Magnetic susceptibility data for powder samples were collected in the temperature range 2–300 K with a Quantum Design SQUID Magnetometer MPMS XL-7. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility. The luminescent spectrum for the crystal solid sample was recorded at room temperature on an LS-55 Perkin Elmer fluorescence spectrophotometer.

2.2. *Synthesis of 1*

To a solution of CuI (0.21 g) in acetonitrile (20 mL) was added solid dppm (1.73 g), giving a colorless solution after stirring for 2 h. To this solution was added solid TCNQ (0.21 g), the resulting solution was further stirred for 1 h and filtered; slow evaporation of the filtrate formed red crystals, collected by filtration, and dried *in vacuo* (0.12 g, 19%). Calcd for $C_{81}H_{68}Cu_3I_2N_2P_6$: C, 57.19; H, 4.00; N, 1.65. Found: C, 57.32; H, 4.01; N, 1.65. IR bands (KBr pellets, cm^{-1}): $\nu = 2182$(s), 2153(s), ν(C≡N); 835 cm^{-1} (w), δ(C–H). ^{31}P NMR (DMF, δ ppm): −13.4; [CH_2Cl_2, λ_{max}/nm (ε/L mol^{-1} cm^{-1})]: 492 (8.37×10^4), 228 (1.92×10^5). Fluorescence spectrum: $\lambda_{ex} = 432$ nm, $\lambda_{em} = 653$ nm.

2.3. *X-ray crystallography*

X-ray diffraction for [$Cu_3(dppm)_3(\mu_3\text{-}I)_2$][(0.5TCNQ)] was performed on a Bruker Smart 1000 CCD diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. All empirical absorption corrections were applied by using SADABS [7]. The structures were solved using direct methods and the corresponding non-hydrogen atoms were refined anisotropically. All hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The hydrogens of water were located in the difference Fourier map and refined isotropically. All calculations were performed using the SHELXTL system [8]. Details of the crystal parameters, data collection and refinement for **1** are listed in table 1 and selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis and characterization*

Reaction of CuI, dppm and TCNQ with a molar ratio of 1 : 1 : 0.5 at room temperature provides red crystals of **1** (yield = 20%), which is air stable in the solid state and soluble in DMF, CH_2Cl_2, and CH_3CN. The ^{31}P NMR spectrum in DMF of **1** exhibits a single resonance at δ −13.4 ppm, showing that the phosphorus atoms are chemically equivalent.

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{81}H_{70}Cu_3I_2N_2OP_6$
Formula weight	1717.63
λ (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	P21/c
Unit cell and dimensions (Å, °)	
a	12.7440(6)
b	28.4796(13)
c	22.6014(11)
α	90
β	103.919(2)
γ	90
V (Å^3)	7962.2(7)
Z	4
D_{Calcd} (Mg m^{-3})	1.433
F(000)	3444
θ range for data collection	1.17 to 25.20°
Reflections collected/unique	82056/14331
Max. and min. transmission	0.7689 and 0.8457
Data/restraints/parameters	14331/3/864
Goodness-of-fit on F^2	0.997
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0780$, $wR_2 = 0.2272$
R indices (all data)	$R_1 = 0.1250$, $wR_2 = 0.2499$

Table 2. Selected bond distances (Å) and angles (°) for **1**.

C(76)–N(2)	1.084(18)	C(78)–N(1)	1.14(2)
Cu(1)–P(6)	2.387(3)	Cu(1)–P(2)	2.389(3)
Cu(1)–I(2)	2.8761(11)	Cu(1)–I(1)	2.9721(12)
Cu(2)–P(3)	2.364(3)	Cu(2)–P(1)	2.365(3)
Cu(2)–I(2)	2.8461(12)	Cu(2)–I(1)	2.8579(12)
Cu(3)–P(4)	2.415(3)	Cu(3)–P(5)	2.419(3)
Cu(3)–I(1)	2.8839(11)	Cu(3)–I(2)	2.9962(13)
P(6)–Cu(1)–P(2)	123.66(11)	P(6)–Cu(1)–I(2)	111.51(7)
P(2)–Cu(1)–I(2)	110.28(7)	P(6)–Cu(1)–I(1)	100.18(7)
P(2)–Cu(1)–I(1)	107.72(7)	I(2)–Cu(1)–I(1)	100.22(4)
P(3)–Cu(2)–P(1)	118.70(10)	P(3)–Cu(2)–I(2)	96.50(7)
P(1)–Cu(2)–I(2)	117.58(8)	P(3)–Cu(2)–I(1)	116.29(8)
P(1)–Cu(2)–I(1)	103.61(7)	I(2)–Cu(2)–I(1)	103.76(4)
P(4)–Cu(3)–P(5)	128.10(10)	P(4)–Cu(3)–I(1)	119.28(7)
P(5)–Cu(3)–I(1)	101.05(7)	P(4)–Cu(3)–I(2)	95.50(8)
P(5)–Cu(3)–I(2)	109.39(8)	I(1)–Cu(3)–I(2)	99.47(4)
Cu(2)–I(1)–Cu(3)	67.52(3)	Cu(2)–I(1)–Cu(1)	63.11(3)
Cu(3)–I(1)–Cu(1)	69.64(3)	Cu(2)–I(2)–Cu(1)	64.48(3)
Cu(2)–I(2)–Cu(3)	66.15(3)	Cu(1)–I(2)–Cu(3)	69.40(3)

IR spectra can be used to assign the oxidation state of TCNQ in its compounds [9]. The ν(C≡N) modes are strongly affected by the metal binding interaction, and δ(C–H) is sensitive to the oxidation state of TCNQ. The infrared spectrum of **1** shows ν(C≡N) stretches at 2181 and 2151 cm^{-1}, lower than free TCNQ (2228 cm^{-1}). The δ(C–H) modes of TCNQ^0 and TCNQ$^-$ occur at ~860 cm^{-1} and between 820–825 cm^{-1}, respectively. Compound **1** exhibits δ(C–H) bending modes at 829 cm^{-1}, suggesting that TCNQ is in the reduced state. The ν(C=C) is also characteristic for TCNQ phenyl rings. The π-bond delocalization over the ring results in one strong (C=C) stretch ranging from 1500 to 1510 cm^{-1} for TCNQ radical ion. **1** exhibits π(C=C) at 1504 cm^{-1}. The color of **1** is red, which is in accord with a TCNQ that is not neutral. The electronic spectral features of reduced TCNQ in the visible region typically give rise to green or red colors due to an intense π–π* transition, the exact energy of which is determined by the degree of charge transfer [10].

3.2. *Electronic spectra*

The electronic spectrum of **1** was recorded in CH_2Cl_2 (figure 1), with main features at 492 nm ($\varepsilon = 8.37 \times 10^4$ L mol^{-1} cm^{-1}) and 228 nm ($\varepsilon = 1.92 \times 10^5$ L mol^{-1} cm^{-1}). The intense feature in the visible region (492 nm) of the spectrum is assigned to a $\pi \rightarrow \pi^*$ transition of a reduced TCNQ [11]. Absorption in the high energy visible region ($\lambda_{max} = 228$ nm) is in accord with the Cu(I)–L transition of a Cu_3 unit.

3.3. *Crystal structure*

Compound **1** crystallizes in space group *P*21/*c*, with four formula units present per unit cell. The structure of **1** consists of one trinuclear $[Cu_3(dppm)_3(\mu_3\text{-}I)_2]^+$ unit, 1/2 isolated $TCNQ^{2-}$ anion, and one water. The structure together with the selected atomic numbering is depicted in figure 2. The three copper atoms form a triangle with a dppm bridging each edge to form a Cu_3P_6 unit. The copper atoms are coordinated to two iodides and two phosphorus atoms of dppm. The I^- are bonded to three copper atoms in a μ_3 fashion from opposite faces of the triangle. The Cu_2P_2C rings adopt envelope conformations with the methylene carbon atoms on the flap, one folded toward one of the faces, and the other two away from it. The disposition of the phenyl rings of dppm is interesting in both cases. The two phenyl rings attached to a phosphorus center stay on

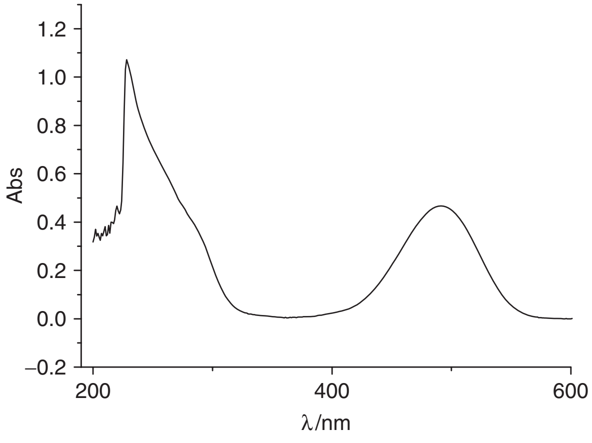

Figure 1. Absorption spectrum of **1** in CH_2Cl_2.

opposite sides of the plane formed by the three copper centers. A selection of important distances and angles in **1** is listed in table 2. The Cu–P distances (2.364(3) to 2.419(3) Å) are longer than observed for $Cu_3(dppm)_3(\mu_3\text{-}I)_2I$ (2.226(9) to 2.269(11) Å) [12] and the Cu–I distances (2.8461(12) to 2.9962(13) Å) are much longer than found in $Cu_3(dppm)_3(\mu_3\text{-}I)_2I$ (2.727(5) to 2.766(5) Å). The average Cu ··· Cu distance (3.196(2) Å) is also longer than that in $Cu_3(dppm)_3(\mu_3\text{-}I)_2I$ (3.165(5) Å).

3.4. *Emission spectra*

At room temperature, **1** exhibits luminescence (figure 3). When excited at 343 nm, **1** showed an emission at 653 nm; free ligands (TCNQ and dppm) did not exhibit emission bands. It is possible that the low-energy emitting state is related to the metal-centered excited state $3d^{10}$ of Cu(I), modified by the copper-copper interactions [13].

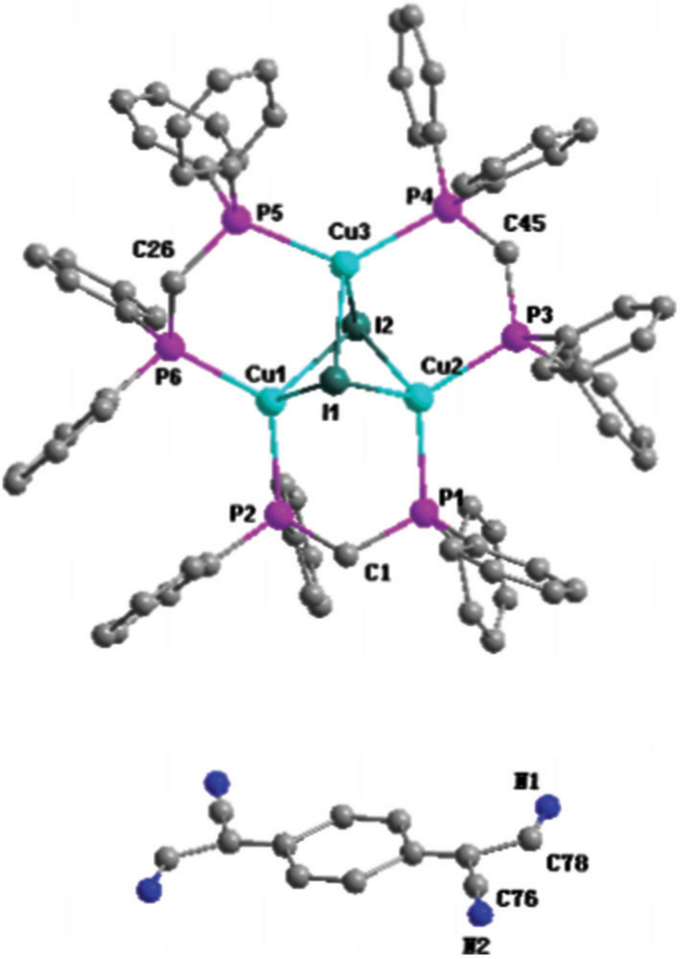

Figure 2. Structure of $[Cu_3(dppm)_3(\mu_3\text{-}I)_2][0.5TCNQ]$ in the crystal of **1**. Hydrogen atoms are omitted for clarity.

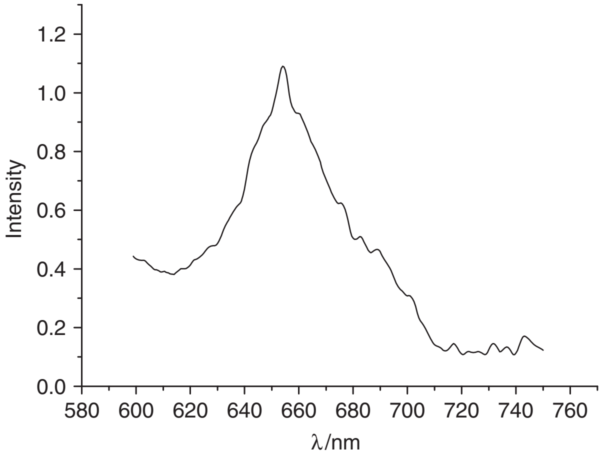

Figure 3. Solid-state emission spectra of **1** at room temperature.

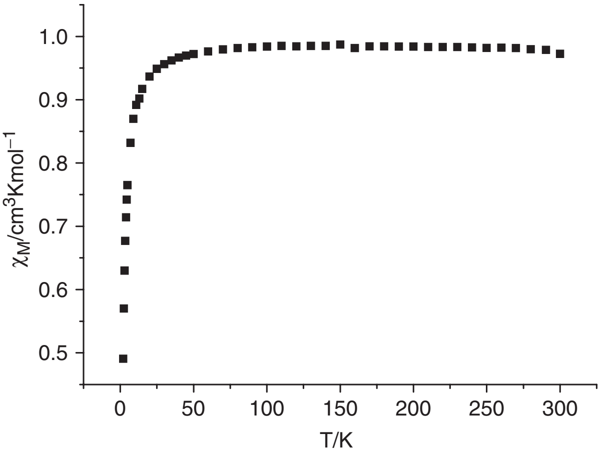

Figure 4. Temperature dependence of $\chi_M T$ at an applied field of 1000 Oe.

3.5. *Magnetic property*

The magnetic properties of **1** are investigated in the temperature range 2–300 K, as shown in figure 4, in the form of $\chi_M T$ *versus* T. The value of $\chi_M T$ at room temperature, 0.98 cm^3 K mol^{-1} (2.80 μ_B), is close to the value of 1.00 cm^3 K mol^{-1} (2.83 μ_B) of a TCNQ^{2-} ion ($S = 1$) and is constant with decreasing temperature, indicating no magnetic coupling between TCNQ^{2-} and Cu_3 unit.

Supplementary data

CCDC 670356 contains the supplementary crystallographic data for this article. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgements

This work was supported by the Research Foundation for Returned Chinese Scholars Overseas of Chinese Education Ministry (No. B7050170). We also thank the South China University of Technology for financial support (grant No. B15-Y1060240, B15-Y1060230 and B15-Y1060340).

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