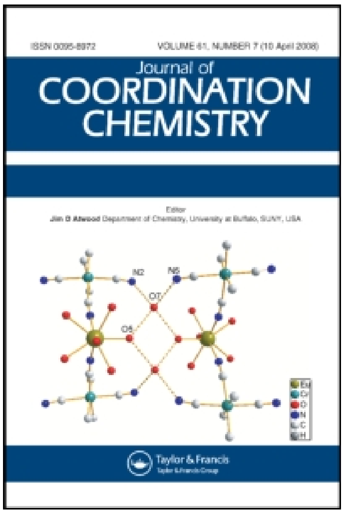

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# {[$Ag_2$ (μ-dppm)$_2$ (μ-TCNQ)$_2$](TCNQ)}, a charge transfer compound derived from a donor with a metal-metal bond

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# {[$Ag_2$ (μ-dppm)$_2$ (μ-TCNQ)$_2$](TCNQ)}, a charge transfer compound derived from a donor with a metal–metal bond

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Reaction of AgNO3, dppm (bis(diphenylphosphino)methane), and TCNQ in molar ratio of 1 : 1 : 1 produced an acceptor–donor silver compound {[$Ag_2$(dppm)$_2$ (μ-TCNQ)$_2$](TCNQ)}, **1**. In the structure, determined by X-ray crystallography, two silver atoms are triply-bridged by two dppm ligands and metal–metal bond to form a dimer; the distance between two Ag is 3.1753(8) Å. Compound **1** was studied by IR and UV/Vis/NIR spectroscopy, exhibiting an intervalence transfer transition at $\lambda = 1286$ nm, and also is photoluminescent ($\lambda_{\max} = 537$ and 654 nm) at room temperature.

*Keywords*: Silver dimer; Charge transfer; Luminescence

## 1. Introduction

Organocyanides such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ), which have low-lying $\pi^*$ orbitals, have played important roles as electron acceptors for "organic metals," enabling the discovery and development of molecule-based materials exhibiting metal-like electrical conductivity [1], superconductivity [2], ferromagnetic ordering [3], and interesting optical properties [4]. In 1985, Shields reported the single-crystal structure of Ag(TCNQ) obtained by electrochemical synthesis [5], which exhibits electric-field-induced bistable switching under certain conditions.

Our interest focuses on the use of electron-poor molecules (TCNE and TCNQ) to react with electron-rich dimetal complexes to prepare d$\pi$–p$\pi$ delocalized systems. Dunbar and co-workers have prepared the "dimer-of-dimers" [{$Re_2Cl_4$(dppm)$_2$}$_2$ (μ-TCNQ)] [6], [{$Ru_2(O_2CCF_3)_4$}$_2$ (μ$_4$-TCNQ)], and {$Rh_2(O_2CCF_3)_4$}$_2$ (μ$_4$-TCNQ)] [7], which exhibit charge transfer between TCNQ and a metal–metal-bonded donor. Herein we report the assembly of $AgNO_3$, bis(diphenylphosphino)methane (dppm) and TCNQ

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to yield an acceptor–donor compound {[$Ag_2$(dppm)$_2$ (μ-TCNQ)$_2$](TCNQ)}, **1**, as well as the structural and spectroscopic characterization of **1**.

## 2. Experimental

$AgNO_3$, dppm, and TCNQ were purchased from commercial sources and used as received.

### 2.1. *Physical measurements*

Infrared spectra were recorded (in the 4000–400 $cm^{-1}$ range) as KBr disks on a Bruker 1600 FTIR spectrometer. Electronic spectra were recorded on a Lambda-900 spectrophotometer from solution in $CH_2Cl_2$. $^{31}$P NMR spectra were measured on a Bruker AM 500 spectrometer in DMF. Chemical shifts are quoted to 85% $H_3PO_4$. 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 $\chi_M$ is the molar magnetic susceptibility. The luminescence spectrum for the crystal was recorded at room temperature on a LS-55 Perkin–Elmer fluorescence spectrophotometer.

### 2.2. *Synthesis of* {*[$Ag_2$(dppm)$_2$ (μ-TCNQ)$_2$](TCNQ)*} *(1)*

$AgNO_3$ (0.170 g, 1 mmol) and dppm (0.384 g, 1 mmol) in methanol (30 mL) were stirred under nitrogen in the dark for 2 h. The solution was then added to TCNQ (0.204 g, 1 mmol) in acetonitrile (10 mL) and the resulting solution was further stirred for 1 h and filtered; slow evaporation of the filtrate formed dark green crystals, collected by filtration, and dried *in vacuo* (0.338 g, 25%). Calcd for $C_{86}H_{56}Ag_2N_{12}P_4$: C, 64.62; H, 3.51; N, 10.52. Found: C, 64.67; H, 3.50; N, 10.51. IR bands (KBr pellets, $cm^{-1}$): $\nu = 2181$ (s) $\nu(C\equiv N)$; 827 $cm^{-1}$ (w) $\delta$(C–H). $^{31}$P NMR (DMF, $\delta$ ppm): $-12.6$; UV-Vis ($CH_2Cl_2$, $\lambda_{max}$ $nm^{-1}$ ($\varepsilon L^{-1} mol^{-1} cm^{-1}$)]: 403 ($7.51 \times 10^4$), 742 ($2.11 \times 10^4$), 842 ($3.91 \times 10^4$), 1284 ($6.0 \times 10^3$). Fluorescence spectrum: $\lambda_{ex} = 480$ nm, $\lambda_{em} = 537$ and 654 nm.

### 2.3. *X-ray crystallography*

Data were collected with a Bruker SMART CCD area detector using graphite monochromated Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å) at room temperature. All empirical absorption corrections were applied by using the SADABS program [8]. The structure was solved using direct methods and the corresponding nonhydrogen atoms were refined anisotropically. All the 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. All calculations were performed using the SHELXTL computer program [9]. 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.

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

| | |
|---|---|
| Empirical formula | $C_{43}H_{28}AgN_6P_2$ |
| Formula weight | 798.52 |
| $\lambda$(Å) | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 11.955(4) |
| $b$ | 13.260(4) |
| $c$ | 14.311(4) |
| $\alpha$ | 109.964(3) |
| $\beta$ | 92.924(3) |
| $\gamma$ | 111.949(3) |
| $V$(Å$^3$) | 1935.7(10) |
| $Z$ | 2 |
| Dc (mgm$^{-3}$) | 1.370 |
| $F$(000) | 810 |
| $\theta$ range for data collection | 2.67–25.50° |
| Reflections collected/unique | 14740/7135 |
| Data/restraints/parameters | 7135/0/469 |
| Goodness-of-fit on $F^2$ | 1.036 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1 = 0.0443$, $wR2 = 0.1274$ |
| $R$ indices (all data) | $R1 = 0.0557$, $wR2 = 0.1372$ |

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

| | | | |
|---|---|---|---|
| Bond distances (Å) | | | |
| Ag(1)–P(2)#1 | 2.4263(10) | Ag(1)–P(1) | 2.4452(11) |
| Ag(1)–N(1) | 2.572(4) | Ag(1)–Ag(1)#1 | 3.1753(8) |
| P(2)–Ag(1)#1 | 2.4263(10) | N(1)–C(26) | 1.146(5) |
| N(2)–C(34) | 1.137(6) | N(3)–C(36) | 1.151(8) |
| N(4)–C(37) | 1.145(8) | N(5)–C(43) | 1.142(5) |
| N(6)–C(42) | 1.129(5) | C(26)–C(27) | 1.430(6) |
| C(27)–C(28) | 1.403(5) | C(27)–C(34) | 1.420(6) |
| C(28)–C(33) | 1.417(5) | C(28)–C(29) | 1.436(5) |
| C(29)–C(30) | 1.359(6) | C(30)–C(31) | 1.420(6) |
| C(31)–C(35) | 1.413(5) | C(31)–C(32) | 1.429(6) |
| C(32)–C(33) | 1.361(5) | C(35)–C(37) | 1.429(8) |
| C(35)–C(36) | 1.429(8) | | |
| Bond angles (°) | | | |
| P(2)#1–Ag(1)–P(1) | 151.73(3) | P(2)#1–Ag(1)–N(1) | 119.23(9) |
| P(1)–Ag(1)–N(1) | 88.46(9) | P(2)#1–Ag(1)–Ag(1)#1 | 86.67(3) |
| P(1)–Ag(1)–Ag(1)#1 | 85.20(3) | N(1)–Ag(1)–Ag(1)#1 | 94.98(10) |

Symmetry transformations used to generate equivalent atoms: #1 $-x, -y, -z$; #2 $-x, -y+2, -z+1$.

## 3. Results and discussion

### 3.1. *Synthesis and characterization*

Reaction between $AgNO_3$, dppm, and TCNQ at 1 : 1 : 1 molar ratio at room temperature provides dark green crystals of **1** (yield = 25%), which is air stable in the solid state, soluble in DMF, $CH_2Cl_2$, and $CH_3CN$.

IR spectra are useful for characterizing TCNQ charge transfer compounds, especially with respect to distinguishing the oxidation state of TCNQ in its compounds [10].

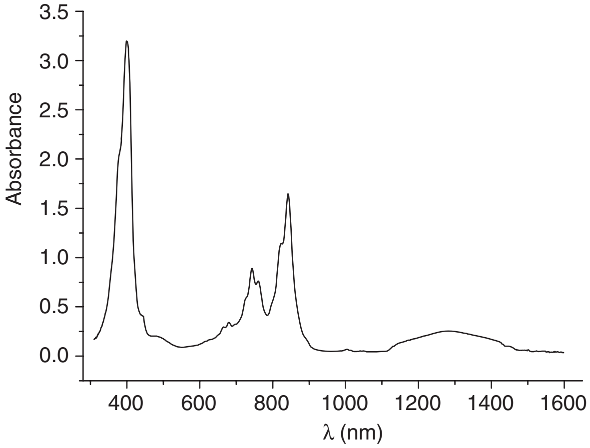

Figure 1. Absorption spectrum of **1** in $CH_2Cl_2$.

IR were measured in solid and $CH_2Cl_2$ solution and the main features are similar. The $\nu(C\equiv N)$ modes are strongly affected by the nature of the metal binding interaction and $\delta$(C–H) is sensitive to the oxidation state of TCNQ. The infrared spectrum of **1** shows one $\nu(C\equiv N)$ stretch at $2181\,cm^{-1}$, lower energy than free TCNQ ($2228\,cm^{-1}$). The shift to lower energy in **1** is in accord with increased $M_2$–TCNQ $\pi$-backbonding for the Ag derivative. The $\pi$-bond delocalization over the ring results in one strong (C = C) stretch ranging from 1500 to $1510\,cm^{-1}$ for $TCNQ^-$ [10]. Compound **1** exhibits $\pi$(C = C) at $1506\,cm^{-1}$. The $\delta$(C–H) modes of $TCNQ^0$ and $TCNQ^-$ occur at $\sim 860\,cm^{-1}$ and between $820–825\,cm^{-1}$, respectively. Compound **1** exhibits $\delta$(C–H) at $827\,cm^{-1}$, suggesting that the TCNQ unit is reduced.

### 3.2. *Electronic spectra*

The electronic spectrum of **1** was recorded in $CH_2Cl_2$ (figure 1), with main features at 403 nm ($\varepsilon = 7.51 \times 10^4$), 742 nm ($\varepsilon = 2.11 \times 10^4$), 842 nm ($\varepsilon = 3.91 \times 10^4$), and 1284 nm ($\varepsilon = 6.0 \times 10^3$). The feature in the near-infrared region of the spectrum is assigned to a metal→TCNQ charge-transfer band (MLCT). Comparing with other TCNQ complexes, the MLCT of **1** is higher than observed for tetranuclear TCNQ complexes of rhenium (680 nm in $CH_2Cl_2$) [11], ruthenium (935 nm in $CH_3CN$) [12a], osmium (1170 nm in $CH_2Cl_2$) [12b], and iron (1008 nm in $CH_2Cl_2$) [12c] but less than for TCNQ complex of manganese (1418 nm in toluene) [12d]. The first three bands ($\lambda_{max} = 403, 742$, and 842 nm) are assigned to the $\pi \rightarrow \pi^*$ transition of a reduced TCNQ ($TCNQ^-$) (free has 842, 761, and 420 nm) [13].

### 3.3. *Crystal structure*

The complex crystallizes in space group $P\bar{1}$, with two formula units present per unit cell. As shown in figure 2, the solid-state structure of **1** consists of a neutral dimeric molecular unit $[Ag_2(\mu\text{-dppm})_2(\mu\text{-TCNQ})_2]$ with the two silvers bridged by a pair of dppm ligands, the metal–metal bond, and a neutral TCNQ. In addition, each silver is

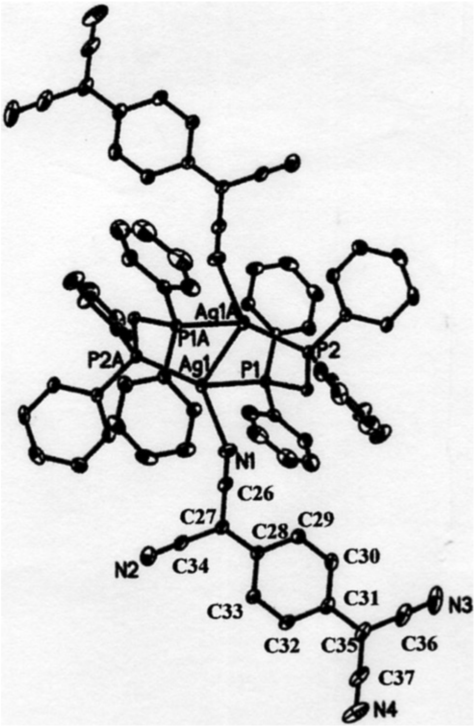

Figure 2. The ORTEP view of [{$Ag_2$(μ-dppm)$_2$}(μ-TCNQ)$_2$].

terminally bound by a single TCNQ anion. The building block [$Ag_2$(μ-dppm)$_2$]$^{2+}$ was linked through the cyanide groups of a bridging TCNQ to form the acceptor–donor compound. Distances and angles within the disilver unit are within the usual observed ranges for derivatives of [$Ag_2$(μ-dppm)$_2$($NO_3$)$_2$] [14]. A selection of important distances and angles in **1** is listed in table 2. The coordination geometry of the two Ag atoms is the same, distorted tetrahedral $AgNP_2$ with $P_2$ from dppm, Ag and one N atom from TCNQ molecule.

The Ag–P distances in **1** of 2.4263(10) and 2.4452(11) Å are in good agreement with the range 2.42–2.44 Å found in [$Ag_2$(μ-dppm)$_2$($NO_3$)$_2$] [14]. The P–Ag–P angle of 151.73(3)° is significantly larger than the corresponding P(1)–Ag–P(2′) angle of 138.3(1)° found in the related dinuclear (dppm)$_2$ compound [$Ag_2$(μ-dppm)$_2$($NO_3$)$_2$] [14]. Two silver atoms are triply bridged by two dppm ligands and the metal–metal bond to form dimer, the distance between silvers is 3.1753(8) Å, which is shorter than the Ag···Ag separation of 3.362(3), 3.356(3), and 3.192(3) Å found in [$Ag_3$(dppm)$_3$$Br_2$]$^+$ [15, 16], but larger than the nonbonding distance of 3.085(1) Å in [$Ag_2$(μ-dppm)$_2$($NO_3$)$_2$] [14]. The silver nitrile bond length in **1** [Ag–N (from TCNQ) = 2.572(4) Å] is larger than that found in Ag(TCNQ) (2.306–2.346 Å) [5]. The silver nitrile bond angle N(1)–Ag(1)–Ag(1)#1 is 94.98(10)°.

The C≡N bond length of **1** is affected by M–N coordination with bridged C≡N bond length of 1.146(5), and the terminal C≡N from 1.137(6) to 1.151(8) Å. For neutral TCNQ in **1**, the average C≡N bond length is 1.136(5) Å.

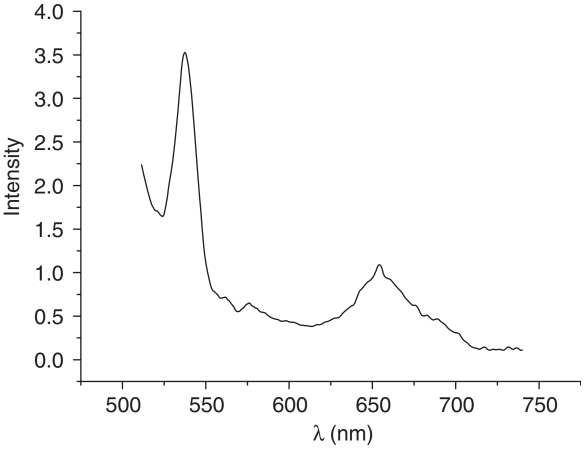

Figure 3. Emission spectrum of **1**.

The C–C distances within the TCNQ ring are good indicators of the oxidation state. The degree of charge transfer from a donor to TCNQ can be estimated by Kistenmacher's method, from the relationship $\rho = A[c/(b+d)] + B$ ($A = -41.667$ and $B = 19.833$), are determined from neutral TCNQ [17] ($\rho = 0$) and RbTCNQ [18] ($\rho = -1$) [19]. The values of $c$, $b$, and $d$ are TCNQ bond lengths. The charges for **1** estimated from the Kistenmacher relation are −0.5643, pointing to partially reduced TCNQ bridges in **1**, which agrees with the IR data in the $\delta$(C–H) region.

### 3.4. *Emission spectra*

$\mathrm{Ag^I}$ complexes may emit photoluminescence at low temperature [20–22] and only a few $\mathrm{Ag^I}$ compounds exhibit luminescence at room temperature [23–25]. The photoluminescence of **1** was investigated in the powdered solid state at room temperature and found to show photoluminescence. At room temperature, the solid-state emission spectra of **1** shows a high-energy band at 537 nm and a lower energy emission at 654 nm (figure 3). The high-energy emission is due to intraligand transition ($\pi \rightarrow \pi^*$ (TCNQ) IT). The low energy is probably associated with a spin-forbidden transition. It is possible that the low-energy emitting state is related to the metal-centered excited state $3d^{10}$ of Ag(I), modified by the silver–silver interaction, due to configuration mixing of the filled d orbital with empty orbitals from the higher 5s and 5p atomic orbitals of the dimeric silver unit (d–s). A more probable assignment of the origin of the low-energy emission involves a TCNQ-to-metal charge transfer (TCNQ→$\mathrm{Ag_2}$ LMCT) excited state.

### 3.5. *Magnetic property*

The magnetic property of **1** is investigated in the temperature range 2–300 K for molar susceptibility. The magnetic behavior of **1** is shown in figure 4 in the form of $\chi_M T$ *versus* $T$. The value of $\chi_M T$ at room temperature, $0.99\,\mathrm{cm^3\,K\,mol^{-1}}$ ($2.82\,\mu_B$), is close to the

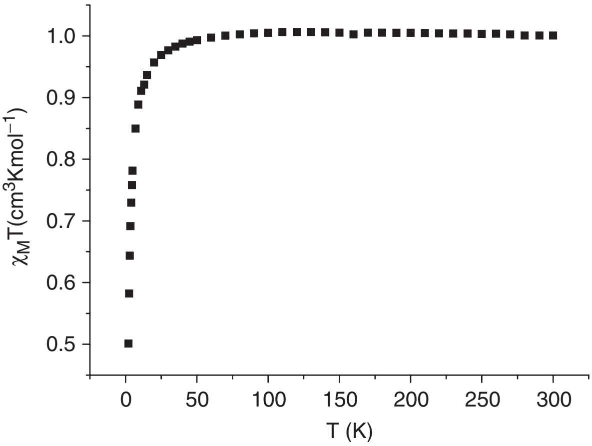

Figure 4. Temperature dependence of $\chi_M T$ at an applied field of 1000 Oe.

value of 1.00 $cm^3$ K $mol^{-1}$ (2.83 $\mu_B$) of two $TCNQ^-$ ions (S = 1/2) and is constant with decreasing temperature, indicating no magnetic coupling between two $TCNQ^-$ via $[Ag_2(dppm)_2]^{2+}$.

In summary, one acceptor–donor compound $\{[Ag_2(dppm)_2(\mu\text{-TCNQ})_2](TCNQ)\}$ has been prepared and exhibits appreciable M–L $\pi$-backbonding. It is photoluminescent ($\lambda_{max} = 537$ and 654 nm) at room temperature.

## Supplementary material

CCDC 666490 contains the supplementary crystallographic data of **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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