

Synthesis and Properties of One-dimensional Heterometal Assemblies [Au(TPP)][M(mnt)₂] (M = Ni, Pt, Au)

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Abstract

Metal complexes of the type [Au(TPP)][M(mnt)₂] (M = Ni, Pt, Au; TPP = tetraphenylporphyrinate ion; mnt = maleonitriledithiolate ion) have been synthesized and characterized. They were presumed to be discrete one-dimensional assemblies based on magnetic, EPR, visible spectral, and conductive investigations. Electric conductivities of the complexes could be expressed by the equation $\sigma = \sigma_0 \exp(-E/kT)$ in the temperature range 303–373 K. The paramagnetic Au–Ni and Au–Pt complexes showed higher electric conductivities and lower activation energies compared with the diamagnetic Au–Au complex, suggesting that the unpaired electron plays an important role in electric conduction of the former complexes.

Introduction

Low-dimensional assemblies of metal complexes are of interest for their physicochemical properties and as new materials such as electric conductors [1]. It is known that some planar metal complexes stack along their molecular axis to form quasi-one-dimensional assemblies. Typical examples are the complexes of phthalocyanine [2], dihydrobenzo-[b,i]-1,4,8,11-tetraazacyclotetradecane [3], glyoximes [4], or dithiomaleonitrile [5]. Partially oxidized tetracyanoplatinate complexes [1, 6, 7] and Magnus' green salt [8–10] are other examples. Magnus' green salt and related complexes exhibit weak metal–metal interactions and it is considered that their linear chain structures are mainly due to the electrostatic attraction between the opposite charges of the constituting complex ions. Thus, the combination of a planar complex cation and a complex anion of dissimilar metal ions affords discrete hetero-

metal assemblies such as [Pt(NH₃)₄][PdCl₄] [11] and [Cu(NH₃)₄][PtCl₄] [12]. This principle must be applicable to the synthesis of other heterometal systems. However, only a few discrete heterometal assemblies have been reported so far, in spite of the great interest in the electric conductivity and magnetism of such systems. In this study we aimed to synthesize new discrete heterometal assemblies of the type [Au(TPP)][M(mnt)₂] (M = Ni, Pt, Au) using tetraphenylporphyrinatogold(III) [Au(TPP)]⁺ as the cationic constituent and dithiomaleonitrato complexes [M(mnt)₂][−] (M = Ni, Pt, Au) as the anionic constituent. This paper deals with the synthesis, characterization, and electric conductivity of the complexes.

Experimental

Preparations

[Au(TPP)][AuCl₄] [13], (NBu₄)[Ni(mnt)₂] [14], (NBu₄)[Pt(mnt)₂] [14], and (NBu₄)[Au(mnt)₂] [14] were obtained by the literature methods.

[Au(TPP)][Ni(mnt)₂]. A solution of (NBu₄)[Ni(mnt)₂] (1.6×10^{-4} mol) in a *N,N*-dimethylformamide(DMF)–acetonitrile(AN) mixture (1:1, 15 cm³) was added to a solution of [Au(TPP)][AuCl₄] (8×10^{-5} mol) in DMF (10 cm³). The mixture was heated for 15 min and then allowed to stand overnight to give red–purple prismatic crystals. They were collected by filtration, washed with DMF, AN, and then ether, and dried over P₂O₅ in a vacuum desiccator. *Anal.* Found: C, 53.68; H, 2.54; N, 9.86. Calc. for C₅₂H₂₈N₈S₄AuNi·H₂O: C, 53.53; H, 2.59; N, 9.60%.

[Au(TPP)][Pt(mnt)₂]. This complex was obtained as red–purple crystals in nearly the same way as that of [Au(TPP)][Ni(mnt)₂] except for the use of (NBu₄)[Pt(mnt)₂] instead of (NBu₄)[Ni(mnt)₂].

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Anal. Found: C, 48.50; H, 2.22; N, 8.76. Calc. for $C_{52}H_{28}N_8S_4AuPt$: C, 48.60; H, 2.20; N, 8.72%.

$[Au(TPP)][Au(mnt)_2]$. This complex was obtained as red crystals in nearly the same way as that of $[Au(TPP)][Ni(mnt)_2]$ using $(NBu_4)[Au(mnt)_2]$ instead of $(NBu_4)[Ni(mnt)_2]$. *Anal.* Found: C, 47.98; H, 2.20; N, 8.61. Calc. for $C_{52}H_{28}N_8S_4Au_2 \cdot H_2O$: C, 47.86; H, 2.32; N, 8.59%.

Measurements

Infrared spectra were recorded on a JASCO IR Spectrometer Model IR-810 on KBr disks or nujol mulls. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrometer Model MPS-5000 or a Shimadzu UV-Vis Spectrometer Model UV-240 in DMF or water or on powder samples. Magnetic susceptibilities were determined by the Faraday method. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$ [15]. Effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_A \times T)^{1/2}$, where χ_A is the magnetic susceptibility corrected for diamagnetism of the constituting atoms. X-band ESR spectra were recorded on powder samples on a JES-FE3X instrument at room temperature. Electric conductivities were measured on pellets in the temperature range 30–100 °C by the usual two-probe method. The instrument used for measurements has been described elsewhere [16]. Samples were pressed into thin disk-shaped pellets (5 mm dia. \times 0.8–1.1 mm t.). In the case of $[Au(TPP)][Ni(mnt)_2]$ and $[Au(TPP)][Pt(mnt)_2]$ the samples were readily solid-shaped under pressure of 4.3×10^2 – 5.7×10^2 bar, however, in the case of $[Au(TPP)][Au(mnt)_2]$ the shaped pellet was easily fractured. Hence, for this specimen the pressure was increased up to 9.7×10^2 bar.

Results and Discussion

Analytical results indicated the general formula of the complexes obtained to be $[Au(TPP)][M(mnt)_2]$, with one molecule of crystal water in the case of $M = Ni$ and Au . The presence of the crystal water was supported by an IR band near 3400 cm^{-1} (nujol mull). The complexes are insoluble in water or alcohols but soluble in DMF or chloroform. Infrared spectra of the complexes resemble each other and contain vibrations due to $[Au(TPP)]^+$ and $[M(mnt)_2]^-$. Attempts to obtain single crystals suitable for X-ray analysis have so far been unsuccessful. Recently, their related complex $[Au(TPP)]_2-[Pt(mnt)_2]$ was structurally analyzed in our laboratory [17]. The result has revealed that the complex has a one-dimensional linear-chain structure (...Au–Pt–Au...Au–Pt–Au...), where the interplane distance between $[Au(TPP)]^+$ and $[Pt(mnt)_2]^{2-}$ is

3.70 Å and the interplane distance between neighbouring $[Au(TPP)]^+$ ions is 3.79 Å. We presume that the present complexes also have a similar one-dimensional structure with alternate stacks of the constituent complex cation and anion.

Synthesis of $[Fe(TPP)][M(mnt)_2]$ was attempted by the reaction of $[Fe(TPP)Cl]$ and $[M(mnt)_2]^-$ in DMF, but the starting materials were always recovered when the reaction mixture was concentrated to a small portion. It is reported that the iron(III) complex of tetraphenylporphyrin always retains a coordination number higher than four with a solvent molecule or a counter ion at the apical position [18]. It is likely that the Fe–Cl bond is strong enough not to permit the stacking of $[Fe(TPP)]^+$ and $[M(mnt)_2]^-$ ions. The synthesis of $[Au(TPP)][Fe(mnt)_2]$ was also attempted by the reaction of $[Au(TPP)][AuCl_4]$ and $(NBu_4)[Fe(mnt)_2]$, but the isolated product by this reaction proved to be $[Au(TPP)][Au(mnt)_2]$. Judging from these facts, it seems that the combination of metal ions with d^8 electronic configuration is one of the prerequisites for constructing one-dimensional heterometal assemblies.

$[Au(TPP)][Ni(mnt)_2]$ and $[Au(TPP)][Pt(mnt)_2]$ are paramagnetic (1.77 and $1.66\ \mu_B$, respectively), while $[Au(TPP)][Au(mnt)_2]$ is diamagnetic. The moments of the former complexes were practically independent of temperature in the range 80–300 K. It is generally known that $[Ni(mnt)_2]^-$ and $[Pt(mnt)_2]^-$ complexes show a subnormal magnetic moment (0.79– $1.54\ \mu_B$ for the Ni complexes and 1.05– $1.15\ \mu_B$ for the Pt complexes) when measured on solid samples [14, 19]. X-ray structural analysis for $\{P(CH_3)(C_6H_5)_3\}[Ni(mnt)_2]$ [20] has demonstrated that a pair of $[Ni(mnt)_2]^-$ anions dimerize through the sulfur atom in the out-of-plane mode and such dimeric units form a one-dimensional infinite chain. Similar chain structures have been found for $(NBu_4)[Cu(mnt)_2]$ [21] and $(NBu_4)[Fe(mnt)_2]$ [22]. Hence, unusual magnetisms of the $[Ni(mnt)_2]^-$ and $[Pt(mnt)_2]^-$ complexes were interpreted in terms of the susceptibility equation for the $(S_1 = 1/2) - (S_2 = 1/2)$ dimer (Bleaney–Bowers equation) [19]. The normal magnetic moment of $[Au(TPP)][Ni(mnt)_2]$ ($1.77\ \mu_B$) and the moment close to the spin-only value of $[Au(TPP)][Pt(mnt)_2]$ ($1.66\ \mu_B$) suggest that the alternate arrangement of $[Au(TPP)]^+$ and $[M(mnt)_2]^-$ is achieved in each crystal and the paramagnetic anion is magnetically diluted.

The EPR spectrum of $[Au(TPP)][Ni(mnt)_2]$ measured on powder sample at room temperature is given in Fig. 1. It exhibits a well-resolved signal of rhombic pattern: $g_1 = 2.10$, $g_2 = 2.05$, and $g_3 = 2.00$. Such EPR spectra have been observed for the $[Ni(mnt)_2]^-$ ion diluted in DMF– $CHCl_3$ glass or in $[Cu(mnt)_2]^-$ [23]. The spectrum of the powder

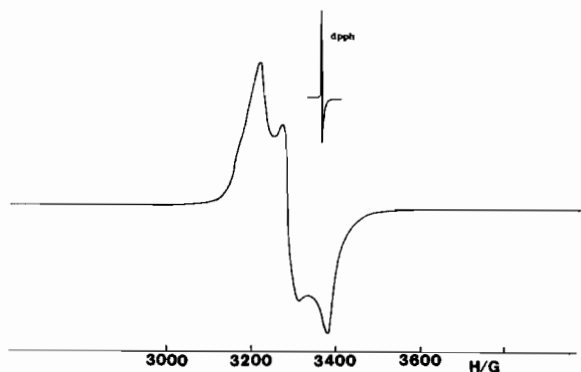


Fig. 1. X-band ESR spectrum of $[\text{Au}(\text{TPP})][\text{Ni}(\text{mnt})_2]$ (powder sample, at room temperature).

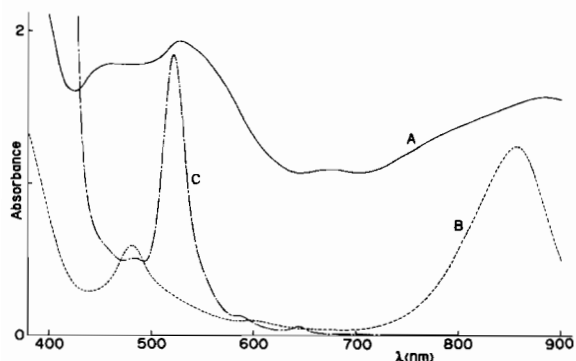


Fig. 2. Reflectance spectrum of: (A) $[\text{Au}(\text{TPP})][\text{Ni}(\text{mnt})_2]$ (given in arbitrary scale), and absorption spectra of: (B) $(\text{NBu}_4)[\text{Ni}(\text{mnt})_2]$ ($2.38 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^{-3}$), and (C) $[\text{Au}(\text{TPP})][\text{AuCl}_4]$ ($1.09 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^{-3}$).

sample of $[\text{Au}(\text{TPP})][\text{Pt}(\text{mnt})_2]$ is somewhat broadened but shows distinct signals at $g \sim 2.09$ and 1.92 . This is essentially the spectrum of $[\text{Pt}(\text{mnt})_2]^-$ diluted in $\text{DMF}-\text{CHCl}_3$ glass [23]. It should be mentioned that no EPR spectra have been reported for the solid samples of $[\text{Ni}(\text{mnt})_2]^-$ and $[\text{Pt}(\text{mnt})_2]^-$ complexes. Therefore, the EPR spectral results add support for the linear-chain structure constructed by the alternate stacking of the complex cation and anion.

The reflectance spectra of $[\text{Au}(\text{TPP})][\text{M}(\text{mnt})_2]$ are shown in Figs. 2–4. For comparison the absorption spectra of their parent complexes are included in each figure.

The spectrum of $[\text{Au}(\text{TPP})][\text{Ni}(\text{mnt})_2]$ is characterized by two main bands at 522 and 880 nm, which correspond to the Soret band of $[\text{Au}(\text{TPP})][\text{AuCl}_4]$ and the 860 nm band of $(\text{NBu}_4)[\text{Ni}(\text{mnt})_2]$, respectively. The 860 nm band of $[\text{Ni}(\text{mnt})_2]^-$ has been assigned to the charge transfer band from the ligand π orbital to the vacant metal d_{xy} orbital [24] or intraligand $\pi-\pi^*$ transition band [25]. Hence, it seems that the spectrum of $[\text{Au}(\text{TPP})][\text{Ni}(\text{mnt})_2]$ is reasonably interpreted by the super-

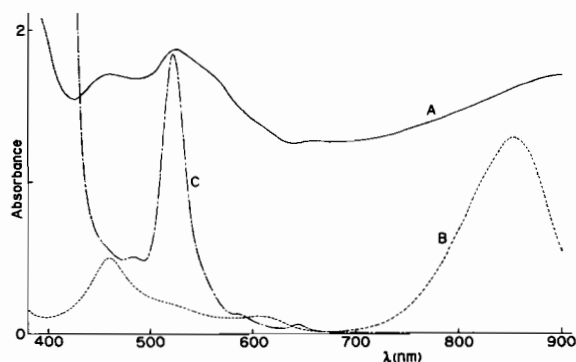


Fig. 3. Reflectance spectrum of: (A) $[\text{Au}(\text{TPP})][\text{Pt}(\text{mnt})_2]$ (given in arbitrary scale), and absorption spectra of: (B) $(\text{NBu}_4)[\text{Pt}(\text{mnt})_2]$ ($1.47 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^{-3}$), and (C) $[\text{Au}(\text{TPP})][\text{AuCl}_4]$ ($1.09 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^{-3}$).

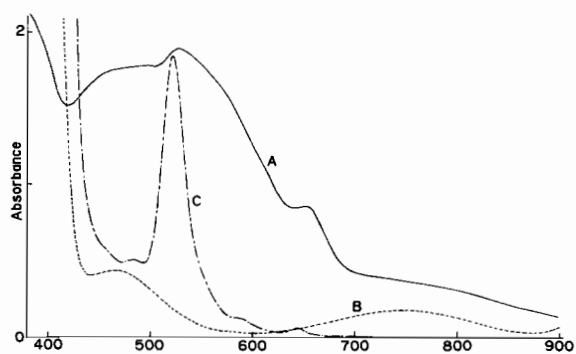


Fig. 4. Reflectance spectra of: (A) $[\text{Au}(\text{TPP})][\text{Au}(\text{mnt})_2]$ (given in arbitrary scale), and absorption spectra of: (B) $(\text{NBu}_4)[\text{Au}(\text{mnt})_2]$ ($4.40 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^{-3}$), and (C) $[\text{Au}(\text{TPP})][\text{AuCl}_4]$ ($1.09 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^{-3}$).

position of the spectra of the constituent complex ions. However, it is seen that the near IR band of the Au–Ni complex is shifted to longer wavelength compared with that of $(\text{NBu}_4)[\text{Ni}(\text{mnt})_2]$ and broadened with a shoulder near 850 nm. This fact implies the presence of an interaction between the constituent complex cation and anion in the crystal. A similar trend in the visible absorption is seen for $[\text{Au}(\text{TPP})][\text{Pt}(\text{mnt})_2]$ also. That is, the CT band of this complex is seen at 898 nm which is located at a longer wavelength compared with that of $(\text{NBu}_4)[\text{Pt}(\text{mnt})_2]$.

The reflectance spectrum of $[\text{Au}(\text{TPP})][\text{Au}(\text{mnt})_2]$ is rather featureless and virtually explainable by the superposition of the spectra of the constituent complex ions. The near IR band (750 nm) is weak in this case, reflecting the electronic configuration $(\pi_1^*)^2(\pi_2^*)^2$ of the $[\text{Au}(\text{mnt})_2]^-$ ion [14].

Electric conductivities were measured on pellets because the complexes did not form large crystals suitable for single-crystal investigations. In order to see the effect of pressure applied during the preparation of the pellet on conductivity, the pellets of

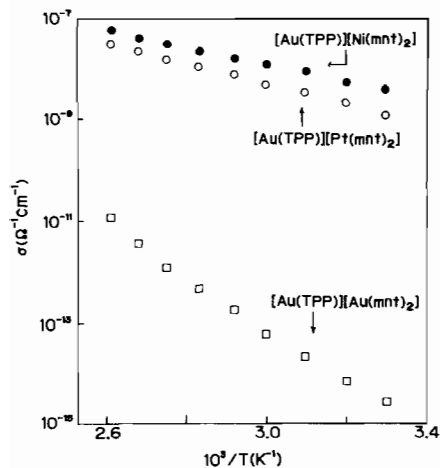


Fig. 5. Temperature variations of electric conductances of the complexes.

$[\text{Au}(\text{TPP})][\text{Ni}(\text{mnt})_2]$ were prepared under 4.3×10^2 and 5.7×10^2 bar. It was found that the change of pressure brought about little effect in the conductivity characteristics. Thus, for $[\text{Au}(\text{TPP})][\text{Ni}(\text{mnt})_2]$ and $[\text{Au}(\text{TPP})][\text{Pt}(\text{mnt})_2]$ the conductivity data were obtained for the pellets solid-shaped under 5.7×10^2 bar. For $[\text{Au}(\text{TPP})][\text{Au}(\text{mnt})_2]$ conductivity data were obtained for the pellet solid-shaped at 9.7×10^2 bar because of the reason mentioned in 'Experimental'. Temperature dependences of electrical conductivities of the complexes are shown in Fig. 5. As seen in the Figure the conductivities increase with the increase of temperature and follow the equation $\sigma = \sigma_0 \exp(-E/kT)$ in the temperature range 30–100 °C (303–373 K), indicating that all the complexes behave as semiconductors with single activation energy E . The magnitude of the specific conductivities observed for $[\text{Au}(\text{TPP})][\text{Ni}(\text{mnt})_2]$ and $[\text{Au}(\text{TPP})][\text{Pt}(\text{mnt})_2]$ (3.97×10^{-9} and $1.09 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ at 30 °C, respectively) are comparable to the values so far reported for $[\text{Ni}(\text{mnt})_2]^-$ and $[\text{Pt}(\text{mnt})_2]^-$ complexes [26–28].

It is to be noted that the present paramagnetic complexes $[\text{Au}(\text{TPP})][\text{Ni}(\text{mnt})_2]$ and $[\text{Au}(\text{TPP})][\text{Pt}(\text{mnt})_2]$ show conductivities of about 10^6 times larger than that of the diamagnetic $[\text{Au}(\text{TPP})][\text{Au}(\text{mnt})_2]$ (at 30 °C). Further, the activation energy E for $[\text{Au}(\text{TPP})][\text{Ni}(\text{mnt})_2]$ and $[\text{Au}(\text{TPP})][\text{Pt}(\text{mnt})_2]$ (0.146 and 0.180 eV, respectively) was found at considerably low levels as compared with the activation energy of $[\text{Au}(\text{TPP})][\text{Au}(\text{mnt})_2]$ (0.449 eV). Hence, it is pointed out from this study that the unpaired electron plays an important role

in electric conductance in the one-dimensional heterometal assemblies.

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