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A novel linear-chain material showing sandwiched stacking via alternative Pt(II)···Pt(II) or Pt(II)···S and π···π interactions

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Abstract

A novel linear-chain material, $[Pt(8\text{-}QNS)_2][Pt(terpy)Cl]_2(ClO_4)_2$ (8-QNS = 8-quinolinethiolate; terpy = 2,2′:6′,2″-terpyridine), has been serendipitously isolated and characterized by a crystallographic study. The title compound composed of alternative cationic $[Pt(terpy)Cl]^+$ pairs and $[Pt(8\text{-}QNS)_2]$ moieties is formed by an interesting rearrangement process, and it shows sandwiched stacking *via* alternative Pt(II)···Pt(II) or Pt(II)···S and π···π interactions.

It is well known that square-planar d^8-metal complexes have a strong tendency to stack in the solid state which shows characteristic optical and electrical properties [1]. The stabilization of these structures is attributed in part to bonding interactions arising from the overlap of the $5d_z^2$ and $6p_z$ orbitals of adjacent metal centers, where the fully occupied $5d_z^2$ levels of adjacent Pt(II) centers split to give bonding (dσ) and antibonding (dσ*) molecular orbitals, and similarly the unoccupied $6p_z$ levels split to give pσ and pσ* orbitals. Configuration interaction (CI) [2] with the pσ and pσ* orbitals stabilizes the dσ and dσ* levels to different extent, respectively, resulting in a net favorable interaction. This description accounts for the solution and solid-state stability, as well as the photophysical properties, of a wide range of stacked complexes with d^8-metal centers, including those of Rh(I), Ir(I) and Pt(II) centers [3]. Taking advantage of the stacking interactions, the "luminescent switch" study pioneered by Mann and coworkers [4] for the detection of volatile organic compounds (VOCs) on absorption and emission spectra of vapochromic Pt(II) and Pd(II) compounds shows that phenomena of luminescent linear-chain materials hold great potential for analytical applications.

When polypyridines such as 2,2′-bipyridine [1a,1e,1g] or 2,2′:6′,2″-terpyridine [1d,1h,5] are used as ligands, a variety of intermolecular interactions of Pt(II) complexes are expected: for example, metal···metal and/or ligand···ligand (π···π) interactions, which are also suggested to be responsible for some intriguing excimeric emissions [6]. While the stacked complexes with the same components are not uncommon, the ones with different components featuring sandwiched stacking are still rare. Here we report the structural properties of a novel linear-chain material composed of cationic $[Pt(terpy)Cl]^+$ pairs and $[Pt(8\text{-}QNS)_2]$ moieties showing sandwiched stacking *via* alternative Pt(II)···Pt(II) or Pt(II)···S and π···π interactions.

Complex **1** was prepared by treating $Pt(terpy)Cl_2 \cdot 2H_2O$ with Na(8-QNS) in a CH_2Cl_2/MeOH solution under a nitrogen atmosphere through an unexpected rearrangement process [7], and its crystal structure has been determined by a crystallographic study [8] as shown in Fig. 1. Half a $[Pt(8\text{-}QNS)_2]$ molecule, one $[Pt(terpy)Cl]^+$ cation and one ClO_4^- anion constitute an asymmetric unit in the crystal lattice of complex **1**, where an interesting structural motif of sandwiched packing has been observed. Pairs of $[Pt(terpy)Cl]^+$ cations alternatively stacked with $[Pt(8\text{-}QNS)_2]$ molecules

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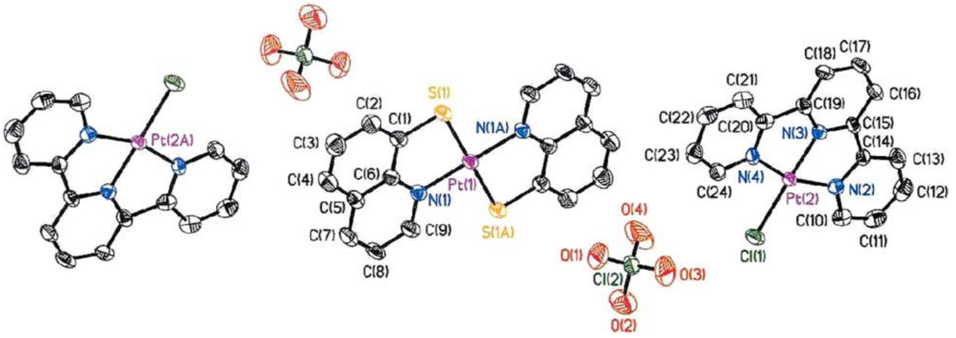

Fig. 1. Molecular structure of **1**. ORTEP diagram shows 30% probability ellipsoids. Selected bond lengths (Å) and angles (°) for **1** : Pt(1)–N(1) 2.022(6), Pt(1)–S(1) 2.303(2), Pt(2)–N(2) 2.006(7), Pt(2)–N(3) 1.913(6), Pt(2)–N(4) 2.002(6), Pt(2)–Cl(1) 2.297(2); N(1)–Pt(1)–S(1) 84.80(19), N(1A)–Pt(1)–S(1) 95.2(2), N(3)–Pt(2)–N(2) 80.8(3), N(3)–Pt(2)–N(4) 81.4(2), N(4)–Pt(2)–N(2) 162.2(3), N(3)–Pt(2)–Cl(1) 178.2(2), N(4)–Pt(2)–Cl(1) 98.3(2), N(2)–Pt(2)–Cl(1) 99.5(2).

form a columnar structure through some intermolecular forces as shown in Fig. 2: for example, Pt(II)$\cdots$Pt(II) or Pt(II)$\cdots$S and $\pi\cdots\pi$ interactions. In the cationic [Pt(terpy)Cl]$^+$ pair, there are a weak Pt(II)$\cdots$Pt(II) interaction with a distance of 3.353 Å in a head-to-tail manner as well as a shortest distance of 3.42 Å between the C (N) and C (N) atoms of the parallel terpy ligands. The 3.353 Å of the Pt(II)$\cdots$Pt(II) distance is within a normal range for the related Pt(II)-terpy complexes [1d,5d,9]. Interestingly, the [Pt(8-QNS)$_2$] molecule intercalated within the cationic [Pt(terpy)Cl]$^+$ pairs shows a weak Pt(II)$\cdots$S interaction with a distance of 3.847 Å (the sum of the van der waal radii is 3.55 Å) [10] and also a shortest distance of 3.55 Å between the C (N) and C (N) atoms of the parallel 8-QNS and terpy ligands. Thus, **1** features a novel linear-chain material showing sandwiched stacking *via* alternative Pt(II)$\cdots$Pt(II) or Pt(II)$\cdots$S interactions, where the $\pi\cdots\pi$ interactions propagate in the whole chain structure. Indeed, **1** can also be regarded as a consequence of intercalating [Pt(8-QNS)$_2$] [11] into a linear-chain [Pt(terpy)Cl]ClO$_4$ [12]. This is reminiscent of the delicate work carried out by Bosnich and co-workers [13] regarding the molecular-recognition study on the structural and spectroscopic properties of double-clipped Pt(II)- or Pd(II)-terpy complexes. Although the cationic [Pt(terpy)Cl]$^+$ pairs remain Pt(II)$\cdots$Pt(II) interactions, the weak Pt(II)$\cdots$S interactions between the [Pt(terpy)Cl]$^+$ and [Pt(8-QNS)$_2$] moieties instead of the metal$\cdots$metal interactions leading to the formation of the columnar structure is somewhat surprised. The strongly luminescent stacked [Pt(terpy)Cl]$^+$ complexes seem to be quenched by the charge-transfer complex of [Pt(8-QNS)$_2$].

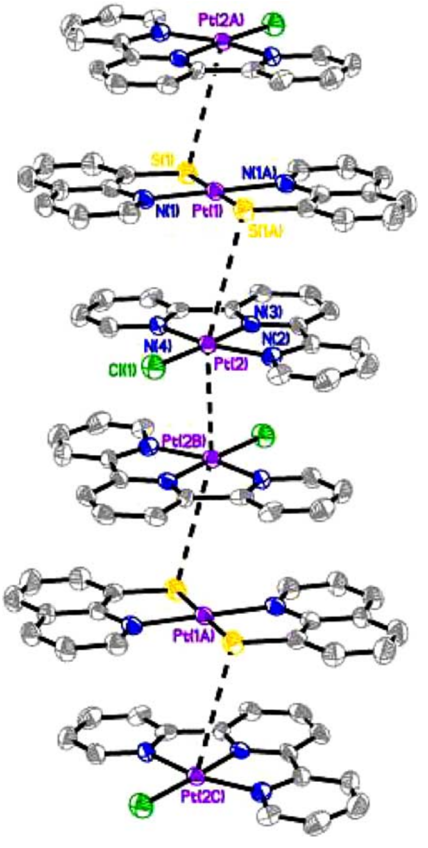

Fig. 2. The molecular packing of **1** shows sandwiched stacking *via* alternative Pt(II)$\cdots$Pt(II) or Pt(II)$\cdots$S and $\pi\cdots\pi$ interactions.

Neutral and cationic Pt(II) species alternative in a stacked array are rare [13], but stacked arrays built from alternative anionic and cationic species are not uncommon, i.e., one-dimensional organic conductors [TTF][TCNQ] (TTF = tetrathiafulvalene; TCNQ = 7,7,8,8-tetra-cyano-*p*-quinodimethane) [14] and related systems [15], where TTF acts as a donor and TCNO an acceptor stacked in an alternative anionic–cationic array. Alternating anion–cation stacking for Pt(II) complexes are also found in [Pt(CN-iso-C$_3$H$_7$)$_4$][M(CN)$_4$] [M = Pt(II) or Pd(II)] [4b], Magnus' Green Salt [16] (MGS, [Pt(NH$_3$)$_4$][Pt(Cl)$_4$]) [17] and [Pt(CNCH$_3$)$_4$][Pd(mnt)$_2$] (mnt = thiomaleonitrile) [18]. Thus, **1** represents a rare example with neutral and cationic species stacked in an alternative array.

A novel linear-chain material, $[Pt(8\text{-}QNS)_2][Pt(terpy)Cl]_2(ClO_4)_2$, has been isolated and characterized by a crystallographic study. Through the unexpected reaction of equimolar $Pt(terpy)Cl_2 \cdot 2H_2O$ and Na(8-QNS), the title compound composed of alternative cationic $[Pt(terpy)Cl]^+$ pairs and $[Pt(8\text{-}QNS)_2]$ moieties is formed by an interesting rearrangement process, and it shows sandwiched stacking *via* alternative Pt(II)$\cdots$Pt(II) or Pt(II)$\cdots$S and $\pi\cdots\pi$ interactions.

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[7] $Pt(8\text{-}QNS)_2][Pt(terpy)Cl]_2(ClO_4)_2$ **1**: The reaction of equimolar Na(8-QNS) [36.6 mg (0.2 mmol), obtained from H8-QNS (39.3 mg, 0.2 mmol) and NaOMe (22.4 mg, 0.4 mmol) in MeOH (25 ml)] with $Pt(terpy)Cl_2 \cdot 2H_2O$ (107 mg, 0.2 mmol) in CH_2Cl_2/MeOH (1:1, 50 ml) at room temperature for 4 h under a nitrogen atmosphere gave a purple-blue solution. Upon addition of $Li(ClO_4)$ the precipitate was filtered off in a vacuum and the resulting solids of **1** isolated as brown perchlorate salts were obtained in a 78% yield with respect to $Pt(terpy)Cl_2 \cdot 2H_2O$. Ether diffusion to a DMF solution of **1** gave black-brown crystals. Anal. Calcd (%) for $C_{48}H_{34}Cl_4N_8O_8Pt_3S_2$: C, 35.11; H, 2.09; N, 6.82. Found (%): C, 35.02; H, 1.75; N, 7.09.

[8] Crystal data for **1**: formula $C_{48}H_{34}Cl_4N_8O_8Pt_3S_2$, m.w. 1642.02, triclinic, space group P-1, $a = 7.8009(4), b = 11.7755(7), c = 13.1108(7)$ Å, $\alpha = 96.2643(13)°$, $\beta = 97.3871(12)°$, $\gamma = 97.2391(12)°$, $V = 1175.18(11)$ Å^3, $Z = 1, D_c = 2.320$ g cm^{-3}, $\mu(\text{Mo-K}_\alpha) = 92.89$ cm^{-1}, $F(000) = 776$. Data collection was carried out on a Bruker SMART CCD diffractometer at 295 K with graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.7107$ Å), 5384 unique reflection ($2\theta < 55°$) were measured and 5384 with $I > 2\sigma(I)$ were used in the refinement. Refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms (332 variables) converged to $R = 0.047$ and $R_w = 0.108$. The final Fourier difference map showed residual extrema in the range of 2.43 to -1.64 eÅ^{-3}.

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