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Synthesis of Lantern-type Dinuclear Mixed-Metal Complex of Platinum(II) and Nickel(II)

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Reaction of tetra(4-methylpyridine-2-thiol)platinum(II) chloride (**1**) with nickel acetate in naphthalene at 120 °C in the presence of potassium hydrogen carbonate affords acetonitriletetra(μ-4-methylpyridine-2-thiolato)platinum(II)nickel(II) (**2**). Structural characterization has been made for **1** and **2**, and confirmed that **2** has a lantern type structure.

The dinuclear Pt(II) complex, where four bridging ligands span two Pt atoms to make Pt•••Pt distance less than 3.0 Å, tends to release two-electrons giving a dinuclear Pt^{III}_2 complex with Pt^{III}—Pt^{III} bond.1) The ease of the oxidation depends on $d_z{}^2$—$d_z{}^2$ overlap: metal—metal distance and electron density on each atom. Tetra(μ-pyridine-2-thiolato)diplatinum(II) ($[Pt(pyt)_4Pt]$), in which Pt•••Pt separation is 2.70 Å, is oxidized to the corresponding Pt^{III}_2 complex, $[XPt(pyt)_4PtX]$, by dissolving it in chloroform.1) The PdPt mixed metal complex $[Pt^{II}(4\text{-mpyt})_4Pd^{II}]$ was oxidized to $[BrPt^{III}(4\text{-mpyt})_4Pd^{III}Br]$ (4-mpyt, 4-methylpyridine-2-thiolate) having Pt^{III}—Pd^{III} single bond.2) In this case, however, chloroform did not serve as oxidant but stronger oxidant such as iodine or bromine was necessary for oxidation. Presumably lesser $5dz^2$—$4dz^2$ than $5dz^2$—$5dz^2$ overlap makes the electron release somewhat difficult as compared with the case of the latter. From this viewpoint, it is of much interest whether $[Ni^{II}(bridge)_4Pt^{II}]$ is oxidized to the corresponding $Ni^{III}Pt^{III}$ complex or not. We have made an effort to prepare the $Ni^{II}Pt^{II}$ precursor, and succeeded in the synthesis of acetonitriletetra(μ-4-methylpyridine-2-thiolato)platinum(II)nickel(II), $[PtNi(4\text{-mpyt})_4(MeCN)]$ (**2**), by use of tetra(4-methylpyridine-2-thiol)platinum(II) chloride, $[Pt(4\text{-mpytH})_4]Cl_2$ (**1**), and naphthalene as platinum source and solvent. This communication reports the preparation, structure and some of the properties of **2**, and also describes the synthesis and structure of the **1**, which is useful for preparation of the lantern type dinuclear Pt(II) complex.

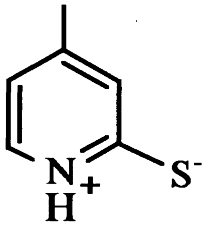
Compound **1** was prepared by refluxing $K_2[PtCl_4]$ and the 4-mpytH in toluene for 20 h. Yellow solid, recrystallized from methanol-dichloromethane, was analyzed to be $[Pt(4\text{-mpytH})_4]Cl_2\cdot MeOH$.3)

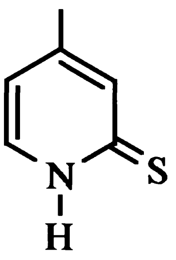
A mixture of $[Pt(4\text{-mpytH})_4]Cl_2$ (767 mg), $Ni(CH_3COO)_2\cdot 4H_2O$ (249 mg), $KHCO_3$ (400 mg) and naphthalene (15 g) in a glass tube was degassed, sealed and then heated to 120 °C. As naphthalene melts with temperature rise, the mixture became a yellow suspension, which turned to red-brown solution by stirring for 1 h at 120 °C. The mixture was cooled and added to *n*-hexane (300 cm^3) with stirring to dissolve naphthalene and then filtered. The orange precipitate was dissolved in dichloromethane and purified by silica gel column chromatography by eluting with acetonitrile-dichloromethane (1:10, v/v). Evaporation of red-brown first eluate gave red crystals of **2**•MeCN in 63% yield.4)

Figure 1 shows the X-ray structure of $[Pt(4\text{-mpytH})_4]Cl_2$.5) The Pt atom has a square-planar coordination by four S atoms. The 4-mpytH ligands are coordinated as twitter ion; i.e. the proton is linked to nitrogen atom and participates in N—H^+•••Cl^- hydrogen bonding, the mean N•••Cl^- distance being 3.11 Å. The chloride ions located above and below the coordination plane do not participate in coordination with Pt atom, as inferred from Pt•••Cl^- distance of 3.612(6) Å.

The **2**•MeCN involves two crystallographically independent molecules (**A** and **B**) in the unit cell.$^{6)}$ They are very similar in structure and therefore one of them is shown in Fig. 2. The Pt atom has a square-planar PtS_4 coordination and the Ni atom has a NiN_5 square-pyramidal coordination with acetonitrile ligand at the apical position, the Ni—NCMe distance being 2.13(2) Å. The Ni atom deviates 0.11 Å in **A** and 0.04 Å in **B**, from the 4 N basal plane toward the MeCN ligand. The mean S—Pt—Ni—N torsion angle and Ni—N—C angle are 29.1° and 161.4°, respectively. The Pt•••Ni distance (Table 1) is significantly shorter than Pt^{II}•••Pt^{II} distance in [Pt(4-mpyt)$_4$Pt] (2.680(2) Å),$^{1)}$ owing to the shorter atomic radius of Ni than that of Pt. The **2**•MeCN is paramagnetic with μ_{eff} = 2.83 B.M. at room temperature.

Of the four Pt—S bonds in **1**•MeOH, two at the cis position are more than 0.03 Å longer than the remainders: i.e. one Pt—S bond is longer than the other in linear S—Pt—S segment. In Pt—S—C segments longer Pt—S bond accompanies shorter S—C bond and *vice versa.* This indicaties the presence of two kinds of the 4-mpytH ligands, each having a greater contribution from either of the two shown below. Ligation of the thiolate and thione donors at trans position may stabilize the PtS_4 coordination, otherwise it would be destabilized by strong mutual trans influence due to the thiolate donors. Similar trend is observed in the Pt—S bond lengths in **2**•MeCN.





Compound **2** showed an irreversible wave with the oxidation and re-reduction peaks at 0.31 and 0.05 V *vs.* Fc^+/Fc in the cyclic voltammogram measured in acetonitrile at 25 °C. The i_c increases with increase of scan rate, suggesting possibility for isolation of the oxidized species at low temperature. Controlled potential coulometry at 0.50 V showed the electrochemical oxidation is of one-electron process. The reaction of orange compound **2** with iodine in dichloromethane at -60 °C affords green solution, from which dark green microcrystalline compound was precipitated by addition of *n*-hexane. Chemical analysis is consistent with the formula of $PtNiI_2$(4-mpyt)$_4$•$2CH_2Cl_2$.$^{7)}$ The UV-visible spectrum resembles that of [Pt_2I_2(4-mpyt)$_4$], though the electronic transitions shift 70—100 nm to lower energy as compared with those of the latter. The Pt($4f_{7/2}$) and Ni($2p_{3/2}$) binding energies were 73.7 and 855.5 eV, respectively.$^{8)}$ These values are 0.9 eV and 0.8 eV higher than the

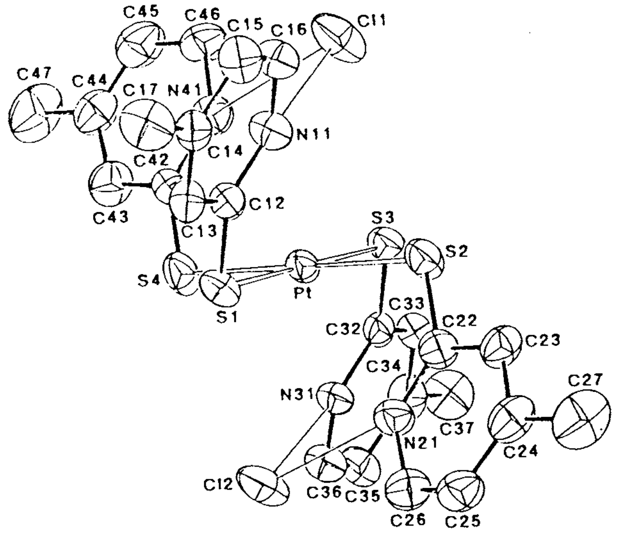


Fig.1. ORTEP drawing of 1 showing 50% probability ellipsoids.

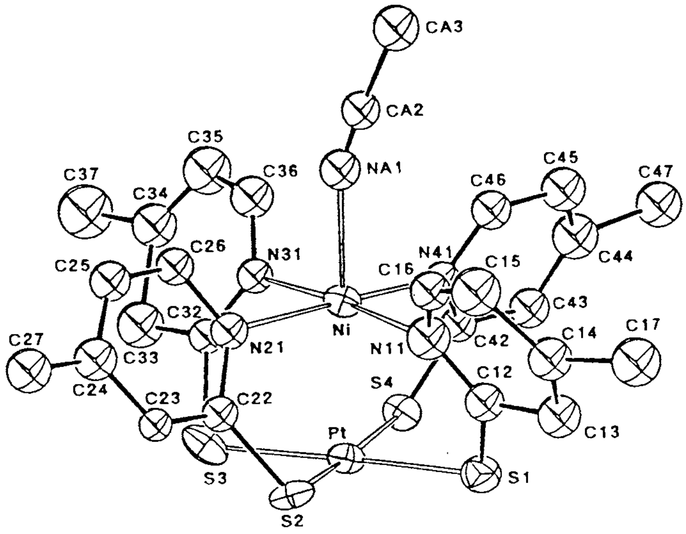


Fig. 2. ORTEP drawing of 2 showing 50% probability ellipsoids.

Table 1. Selected Bond Lengths (Å)

	1•MeOH	2•MeCN	
		A	B
Pt•••Ni		2.545(4)	2.534(4)
Pt—S(1)	2.305(5)	2.27(1)	2.27(1)
S(2)	2.312(5)	2.32(1)	2.22(1)
S(3)	2.350(5)	2.38(1)	2.36(1)
S(4)	2.332(5)	2.41(1)	2.34(1)
Ni—N(1)		2.17(2)	2.30(2)
N(2)		2.23(2)	2.25(2)
N(3)		2.05(2)	2.12(2)
N(4)		1.98(2)	1.99(2)
S(1)—C(12)	1.75(2)		
S(2)—C(22)	1.76(2)		
S(3)—C(32)	1.68(2)		
S(4)—C(42)	1.70(2)		

corresponding ones in **2** (72.8 eV for Pt($4f_{7/2}$), 854.7 eV for Ni($2p_{3/2}$)), suggesting that both metal atoms in the dark green compound are or either one is in higher oxidation state than those in **2**. Crystallization of the reaction product with iodine is underway.

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References

1) K. Umakoshi, I. Kinoshita, A. Ichimura, and S. Ooi, *Inorg.Chem.*, **26**, 3551 (1987); D. M. Roundhill, H. B. Gray, and C-.M. Che, *Acc. Chem. Res.*, **22**, 55 (1989) and references therein.

2) T.Toyoshima, I. Kinoshita, K. Kitano, A. Ichimura, K. Umakoshi, and S. Ooi, unpublished work.

3) Anal. Found: C, 37.59; H, 3.68; N, 7.31%. Calcd for $C_{25}H_{32}N_4S_4OPtCl_2$: C, 35.97; H, 3.80; N, 7.00%.

4) Anal. Found: C, 40.20; H, 3.59; N, 10.03%. Calcd for $C_{28}H_{30}N_6S_4NiPt$: C, 40.39; H, 3.63; N, 10.10%.

5) Crystal Data: FW = 798.78, triclinic, space group $P1$, a = 10.923(1), b = 10.318(1),c = 7.995(1) Å, α = 108.18(1)°, β = 90.96(1)°, γ = 98.50(1)°, μ(MoK_α) = 46.2 cm^{-1}, d_c = 1.57 g cm^{-3}, Z = 1. A total of 2552 intensities ($F_o^2 \geq 3\sigma(F_o^2)$) were collected on an automated diffractometer by use of graphite-monochromated MoK_α radiation and they were corrected for absorption. The structure was refined by least-squares method, minimized function being $\Sigma w(|F_o| - |F_c|)^2$ where $w = \sigma(F_o^2)^{-2}$. The structure refinement on the assumption of $P\bar{1}$ space group reduced R value to 0.052 but gave no further improvement. The space group $P1$ was employed in the subsequent refinements which led to a convergence with R = 0.034.

6) Crystal Data: FW = 832.60, orthorhombic, space group $P2_12_12_1$, a = 16.603(1), b = 21.343(1), c = 18.220(1) Å, μ(MoK_α) = 52.4 cm^{-1}, d_c= 1.71 g cm^{-3}, Z= 8. A total of 4362 intensities ($F_o^2 \geq 3\sigma(F_o^2)$) were collected on an automated diffractometer by use of the MoK_α radiation. Correction was made for absorption. The structure was solved by the Patterson-Fourier method and refined by the least-squares to R = 0.064.

7) Anal. Found: C, 26.04; H, 2.31; N, 5.41%. Calcd for $C_{26}H_{28}N_4S_4Cl_2I_2NiPt$: C, 26.60; H, 2.41; N, 4.77%.

8) XPS data were collected on a VG SCIENTIFIC ESCALAB MKII spectrometer. The binding energies were those based on IE[C(1s)] = 285.0 eV.

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