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Crystal Structure of 2-Fluoroacetamidato-Bridged Mixed-Valent Octanuclear Platinum Blue with Average Platinum Oxidation State of 2.08, $[Pt_8(NH_3)_{16}(CH_2FCONH)_8](NO_3)_{8.66} \cdot 4H_2O$

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Red-purple plate crystals of $[Pt_8(NH_3)_{16}(CH_2FCONH)_8](NO_3)_{8.66} \cdot 4H_2O$ have been prepared and the crystal structure is reported. Magnetic susceptibility measurement revealed that the compound is a mixture of $[Pt(2.0+)_8(NH_3)_{16}(CH_2FCONH)_8]^{8+}$ ($Pt(2.0+)_8$) and $[Pt(2.125+)_8(NH_3)_{16}(CH_2FCONH)_8]^{9+}$ ($Pt(2.125+)_8$), and the mixed ratio is $Pt(2.125)_8/Pt(2.0+)_8=1.97$.

The authors have studied a class of mixed-valent platinum compounds with amidate ligands. By using acetamidate ligand, an octaplatinum compound $[Pt(II)_6Pt(III)_2(NH_3)_{16}(CH_3CONH)_8]^{10+}$ with the average platinum oxidation state of 2.25 was obtained.$^{1)}$ The two unpaired electrons of the two Pt(III) atoms are diamagnetically coupled and the compound is diamagnetic. In the present study, we have prepared a similar class of compound with 2-fluoroacetamide as the bridging ligand, in order to discuss the differences of the structures, the magnetic properties and the redox properties, which might be affected by the electron-withdrawing nature of the fluorine atom. The compound obtained was $[Pt(2.08+)_8(NH_3)_{16}(CH_2FCONH)_8](NO_3)_{8.66} \cdot 4H_2O$ which was the same structure but has a lower average Pt oxidation state.

The 2-fluoroacetamidate complex was prepared as follows: an aqueous solution of 1 mmol of cis-$[Pt(NH_3)_2(OH_2)_2](NO_3)_2$ was prepared according to the previous method.$^{1)}$ To the solution 0.077 g (1 mmol) of 2-fluoroacetamide was added and the solution was reacted at 40 ℃ for two and a half days. After the solution was stored at 5 ℃ for 2 days, red-purple plate crystals appeared. Anal. Found: C, 6.49; H, 2.39; N, 14.60%. Calcd for $[Pt_8(NH_3)_{16}(CH_2FCONH)_8](NO_3)_{8.66}$ $4H_2O$: C, 6.30; H, 2.64; N, 15.05%.

A crystal of approximate dimensions of 0.13 x 0.13 x 0.03 mm^3 was used for X-ray crystallographic study. Since the crystal is not stable to

X-ray radiation, it was coated with a polymer film. The crystal data are as follows: FM = 3050.8, triclinic, space group $P\bar{1}$, a=12.214(5), b=15.517(9), c=10.794(4) Å, α=106.85(4)°, β=97.92(3)°, γ=103.01(4)°, V=1862(2) Å^3, D(calcd)=2.72 g/cm^3, D(measd)=2.83 g/cm^3 and Z=1. The X-ray diffraction intensities were collected in the range of $3° < 2\theta < 40°$ on a Rigaku AFC-5R diffractometer with graphite monochromated Mo Kα radiation. Analytical deterioration and absorption corrections have been applied to the data. A total of 2069 independent reflections with $|Fo| > 4\sigma(|Fo|)$ corrected for Lorentz and polarization effects were used for the calculation. The structure was solved by a direct method. Only Pt and F atoms were treated anisotropically and the rest non-hydrogen atoms were treated isotropically. Full-matrix least-squares refinement of the structure with 226 parameters converged to R=0.096 and R_w=0.106 ($w=1/\sigma^2(Fo)$).

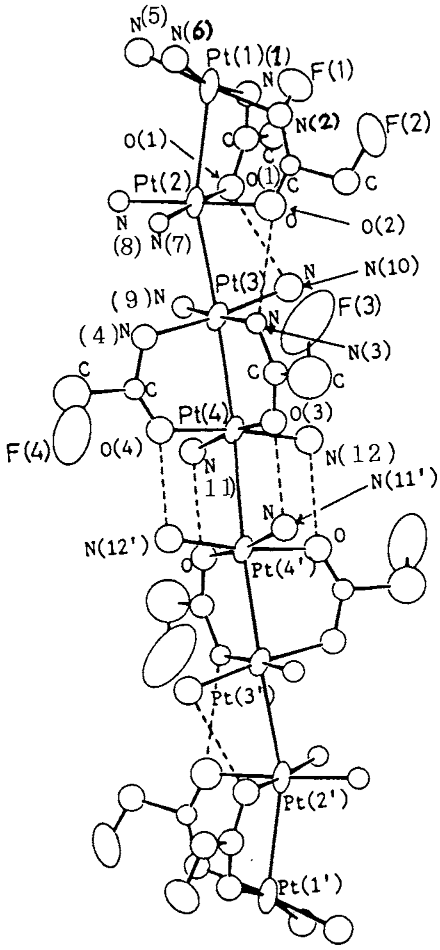

Fig. 1. The structure of $[Pt(2.08+)_8(NH_3)_{16}(CH_2FCONH)_8]^{8.66+}$.

The structure of the complex cation is shown in Fig. 1. The structure is basically the same as that of the previously reported acetamidate-bridged octanuclear Pt compound, $[Pt(2.25+)_8(NH_3)_{16}(CH_3CONH)_8](NO_3)_{10} \cdot 4H_2O$,$^{1)}$ however the average Pt oxidation state is different as shown by the formula. The selected Pt-Pt distances and angles, and the distances of the inter-ligands hydrogen bondings are listed in Table 1.

The Pt-Pt distances in the previously reported acetamidate compound$^{1)}$ are; Pt(1)-Pt(2)=2.880(2), Pt(2)-Pt(3)=2.900(1), Pt(3)-Pt(4)=2.778(1) and Pt(4)-Pt(4')=2.934(1) Å, and therefore all the corresponding distances are longer by 0.045 - 0.062 Å in the present complex. This fact is the result of a lower average Pt oxidation state of the present complex. A similar relation between the average Pt oxidation state and the Pt-Pt

Table 1. Selected interatomic distances(Å) and angels(deg)

Pt-Pt distances	
Pt(1)-Pt(2)	2.938(5)
Pt(2)-Pt(3)	2.962(5)
Pt(3)-Pt(4)	2.835(5)
Pt(4)-Pt(4')	2.979(5)

Pt-Pt-Pt angles	
Pt(1)-Pt(2)-Pt(3)	161.8(1)
Pt(2)-Pt(3)-Pt(4)	166.4(2)
Pt(3)-Pt(4)-Pt(4')	169.5(1)

Intramolecular hydrogen bondings	
O(1)-N(9)	3.25(7)
O(1)-N(10)	2.91(8)
O(2)-N(3)	2.94(8)
O(2)-N(10)	3.23(10)
O(3)-N(11')	2.66(8)
O(4)-N(12')	2.74(8)

Coordination spheres	
Pt(1)-N(1)	2.12(6)
Pt(1)-N(2)	2.09(7)
Pt(1)-N(5)	2.21(7)
Pt(1)-N(6)	2.07(6)
Pt(2)-O(1)	2.07(4)
Pt(2)-O(2)	2.10(7)
Pt(2)-N(7)	2.05(4)
Pt(2)-N(8)	2.11(6)
Pt(3)-N(3)	2.10(6)
Pt(3)-N(4)	2.06(5)
Pt(3)-N(9)	2.00(6)
Pt(3)-N(10)	2.01(5)
Pt(4)-O(3)	1.94(6)
Pt(4)-O(4)	2.03(4)
Pt(4)-N(11)	2.00(7)
Pt(4)-N(12)	2.07(5)

distance is observed in amidate-bridged tetranuclear platinum-blue compounds.[2-4)]

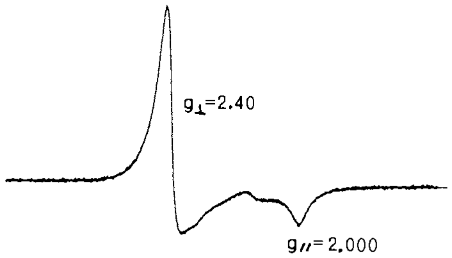

Fig. 2. An ESR spectrum of $[Pt(2.08+)_8(NH_3)_{16}(CH_2FCONH)_8](NO_3)_{8.66} \cdot 4H_2O$ in the solid state at 300 K.

The ESR spectrum measured with a microcrystalline sample is shown in Fig. 2. The spectrum is consistent with a single unpaired electron per molecule and the unpaired electron resides in dz^2 orbitals. However, the integrated intensity of the signal per molecule is only ca. 68% of that for the previously reported tetranuclear platinum blue with one unpaired electron and α-pyridonate ligands, $[Pt(2.25+)_4(NH_3)_8(C_5H_4NO)_4]^{5+}$,[5)] whose spectrum was obtained on the same ESR conditions. From these facts it is inferred that the non-oxidized isostructural but diamagnetic $Pt(2.0+)_8$ complex would be partially mixed in the paramagnetic $Pt(2.125+)_8$ complex. Magnetic susceptibility measurement of the compound on a vibrating-sample magnetometer (Princeton Apllied Research, Model 4500) shows that the compound obeys simple Curie paramagnetism down to 4.2 K. The obtained magnetic moment of μ_{eff}=1.41 B.M. also provides the weight percentage of $Pt(2.125)_8$ complex to be 65.77%, which is consistent with the result of the ESR study. Thus, the present compound can be regarded as a mixture of diamagnetic $Pt(2.0+)_8$ and paramagnetic $Pt(2.125+)_8$ complexes. This is the first report of a paramagnetic octanuclear platinum complex and is contrasted to the previously reported diamagnetic acetamidate-bridged $Pt(2.25+)_8$ compound.1) A similar mixture of tetranuclear compounds with different average Pt oxidation states has been reported.3) The formula and the non-stoichiometric number of the nitrate groups in the present compound have been determined based on the magnetic measurement. X-Ray diffraction analysis of the present compound shows the existence of 6 nitrate groups per octanuclear complex and the remaining nitrate ions seem to be disordered in the crystal lattice. The samples used for the X-ray analysis and for the magnetic measurement were identical, which was confirmed with elemental analysis. In comparison with an acetamidate $Pt(2.25+)_8$ complex, the lower average Pt oxidation state of 2.08+ would be a result of the higher redox potential of the present compound, which can be reasonably explained by the poorer donor ability of the 2-fluoroacetamidate. In fact, the 2-fluoroacetamidate compound shows an oxidation wave at 0.61 V vs. SCE, which is 0.08 V higher than that of the acetamidate compound, and therefore, is relatively resistant to oxidation.

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