Synthesis of 2,2'-dipyridylamine (Hdpa)

The mixture of 10g 2-aminopyridine and 20g potassium tert-butyl alcohol with 200ml benzene as the solvent were put in a 500ml flask and refluxed. 10ml 2-chloropyridine was added to the reaction mixture 2 hours later and continued to refluxing for 72 hours. Remove benzene using rotary evaporator after cooling and added 100ml H_2O and 150ml CH_2Cl_2 to the reddish brown product. Extracted CH_2Cl_2 layer and extracted several times using 100ml CH_2Cl_2 and anhydrous magnesium sulfate was added to the CH_2Cl_2 solution staying for 24h to remove water. Filtrating magnesium sulfate and removed CH_2Cl_2 using rotary evaporator and reddish brown crystals were obtained by recrystalizing using CH_2Cl_2/n-hexane.

Synthesis of $Ni_3(dpa)_4Cl_2$

Hdpa (1.36 g, 8mmol), $NiCl_2 \cdot 6H_2O$ (1.44 g, 6mmol) and naphthalene (14.4g) were placed in an Erlenmejer flask. After stirring the mixture at 160□ for 10min, 3ml Butanol was added and continued heating until complete evaporation of water and n-butanol. Then 0.88g(8mmol) tert-butyl alcohol in 15ml n-butanol was slowly added to the mixture. Continuing heating at 160℃ till the mixture changed to purple and added n-hexane after cooling to extract naphthalene. Purple crystals were obtained from CH_2Cl_2/n-hexane.

Synthesis of $Ni_3(dpa)_4(ClO)_2$

$AgClO_4$(0.447g, 2.2mmol) in 5ml CH_3OH was added to a solution of $[Ni_3(dpa)_4Cl_2]$(1.0g, 1.1mmol)in 50ml CH_2Cl_2 at room temperature and stirred for 10min and then filtered the precipitation. The filtrate was rotary evaporated and recrystallized by CH_2Cl_2/n-hexane and purple crystals were obtained. IR (KBr, cm^{-1}): 3434w, 1604s, 1594s, 1550m, 1469s, 1425s, 1358s, 1313m, 1285m, 1242w, 1154s, 1116s, 1088s, 1014m, 927w, 894w, 764s, 744m, 637m, 627m, 518w.

Table S1. Parameters of Ni-Ni, Ni-O, Ni-N, and Ni-Ni-Ni angles in complexes **1**-**3**.

Bond	Complex **1**	Complex **2**	Complex **3**
Ni1-Ni2	2.4118(8)	2.4409(12)	2.4359(7)
Ni2-Ni3	2.4144(8)	2.4295(12)	2.4213(8)
Ni4-Ni5, Ni5-Ni6		2.4458（11）	2.4396(7)
		2.4326（11）	2.4532(7)
Ni-O	2.028(4)	1.997(5)	2.017(3)
	2.037(3)	2.004(5)	2.016(3)
		2.007(4)	2.039(3)
		1.988(5)	2.020(3)
Ni-N	2.103(4)-2.081(4)	2.144(5)-2.062(6)	2.118(4)-2.058(4)
	1.907(4)-1.893(4)	1.903(5)-1.885(5)	1.904(4)-1.892(3)
Ni-Ni-Ni	179.48(3)	179.26(5)	178.10(3)
		177.75(5)	178.96(3)

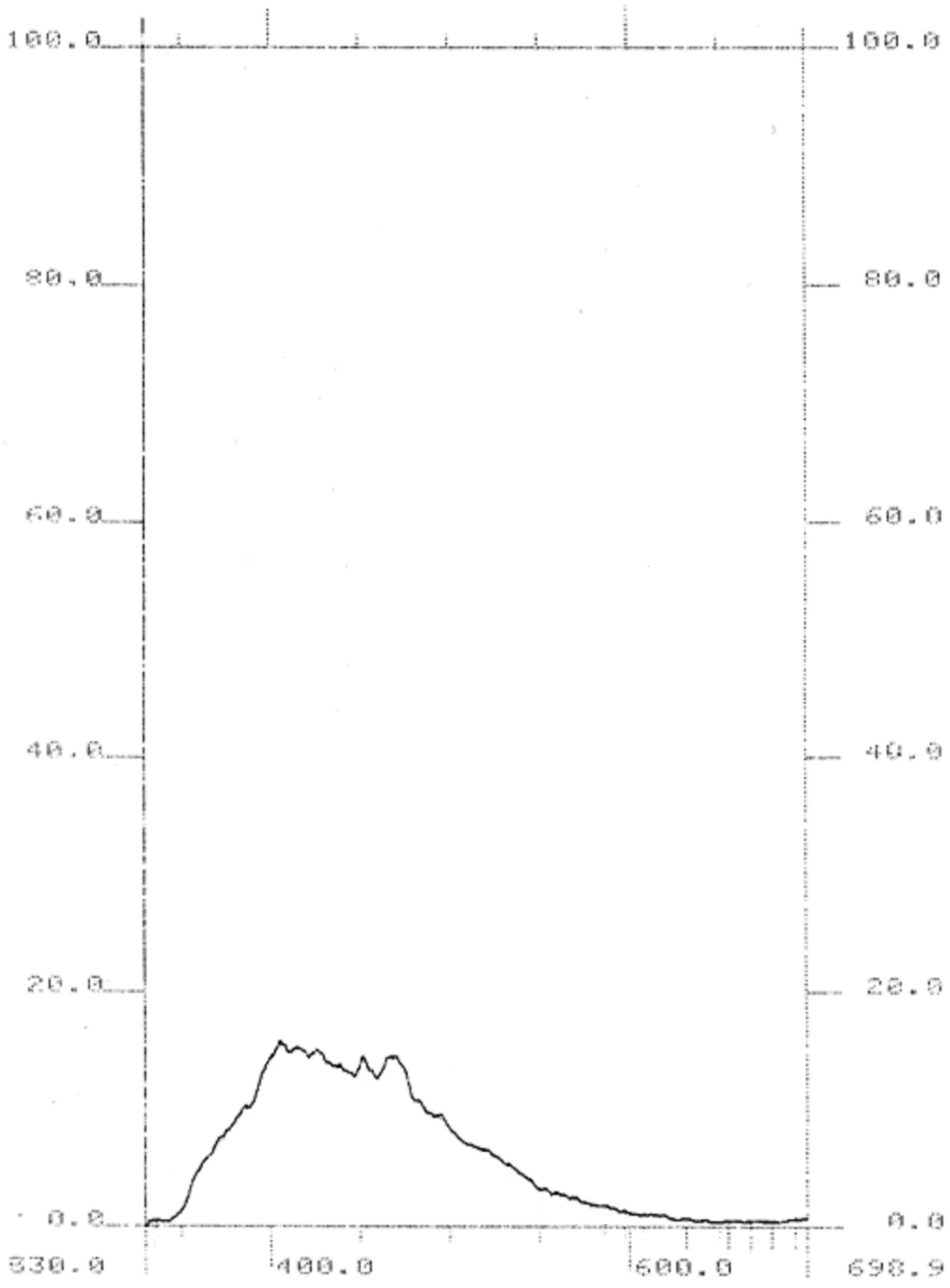

Figure S1. Fluorescent spectrum for complex **1**.

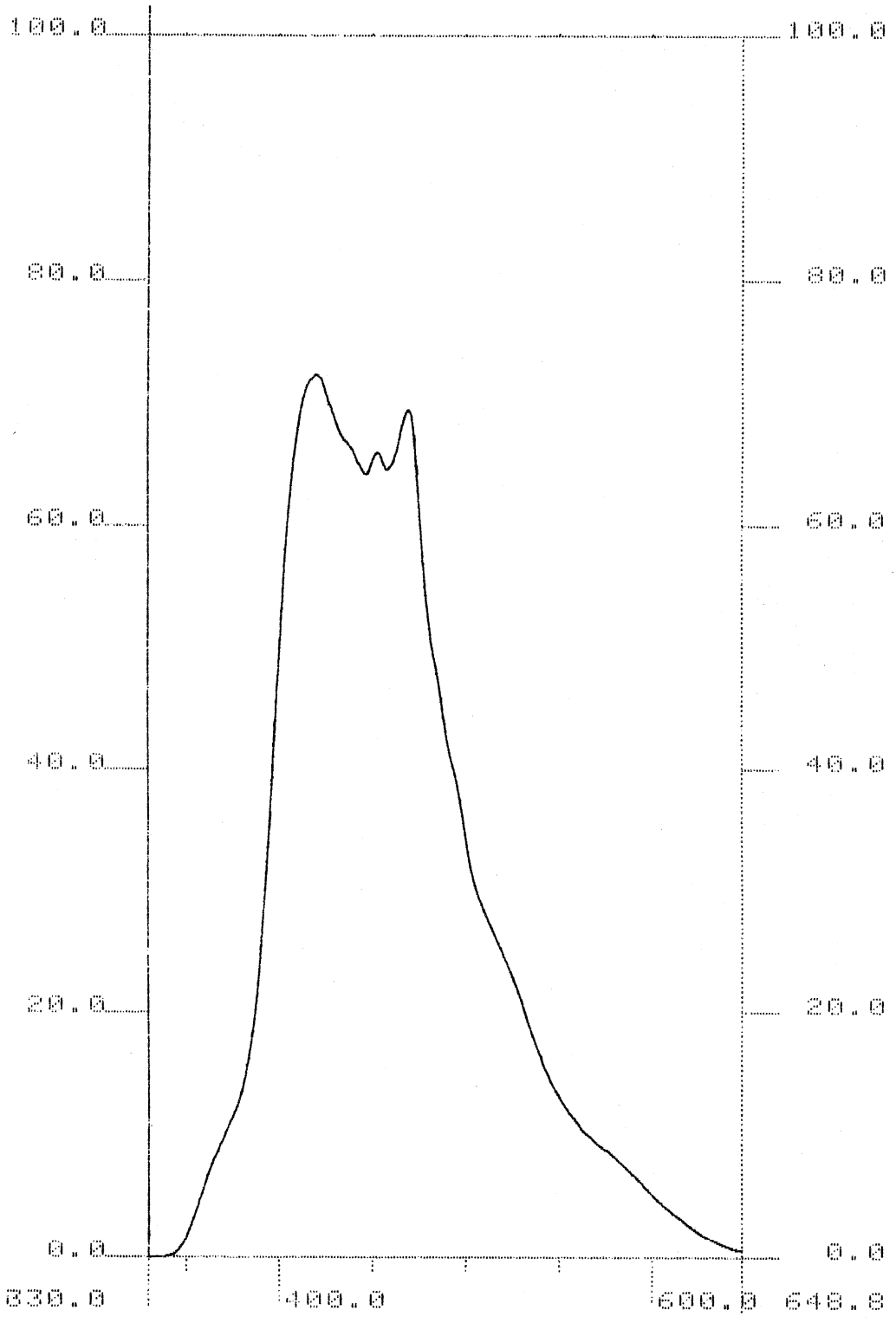

Figure S2. Fluorescent spectrum of complex **2**.

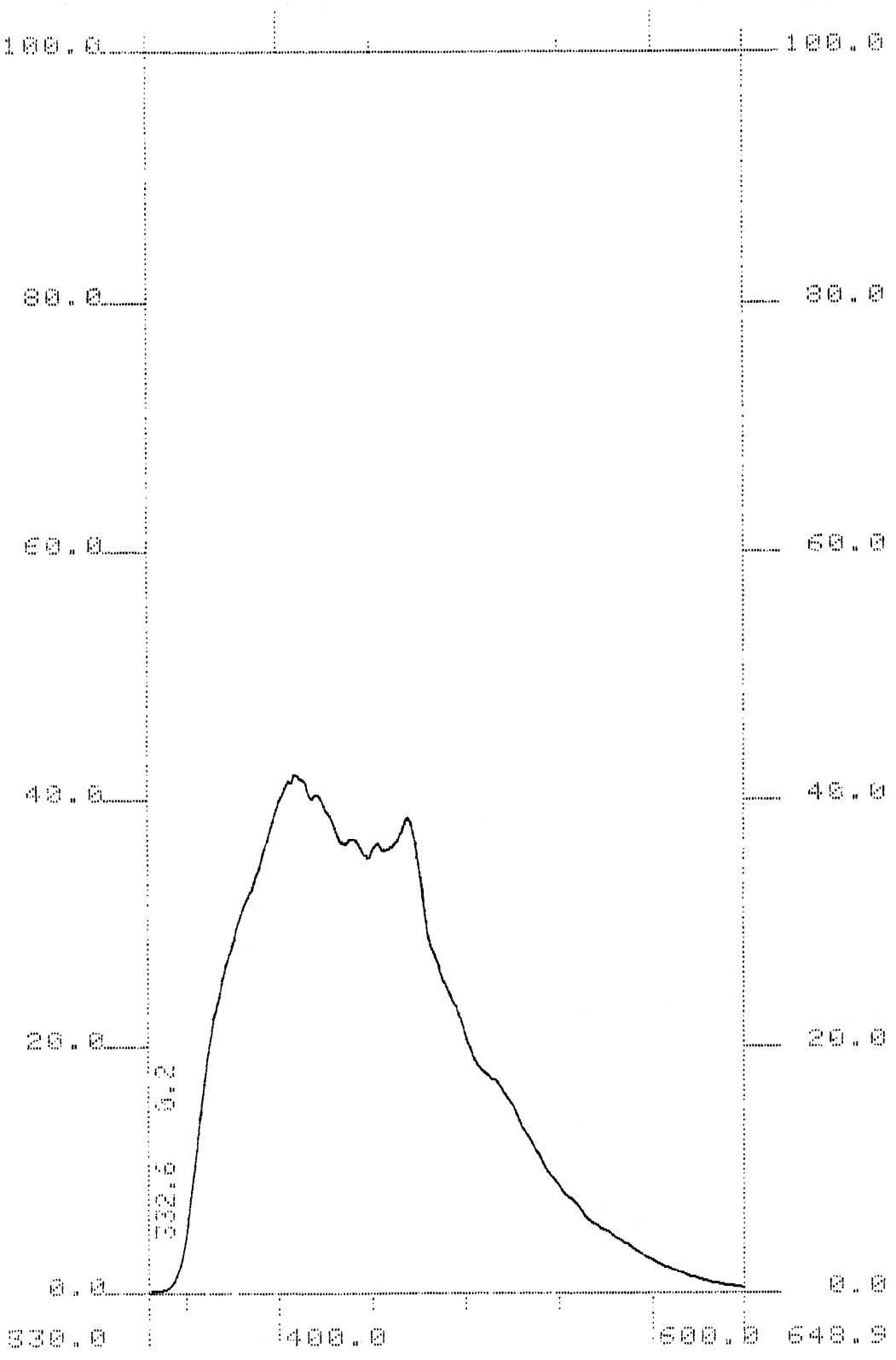

Figure S3. The fluorescent spectrum of complex **3**.