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Infrared Spectrum of Nitro(5,10,15,20-tetraphenylporphyrinato)(piperidine)cobalt(III)

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The infrared (IR) spectrum of nitro(5,10,15,20-tetraphenylporphyrinato)(piperidine)cobalt(III) is measured in the 2000-500 cm^{-1} region. The band at 1420 cm^{-1} is assigned as the asymmetric stretching vibration of the nitro group.

Nitrosyl(5,10,15,20-tetraphenylporphyrinato)cobalt(II) ([Co^{II}(tpp)(NO)])$^{1)}$ reacts with molecular oxygen in the presence of piperidine to give nitro(5,10,15,20-tetraphenylporphyrinato)(piperidine)cobalt(III) ([Co^{III}(tpp)(pip)(NO$_2$)], (**1**)).$^{2)}$ The IR spectrum of **1** in the 2000-500 cm^{-1} region and band assignments of the nitro group$^{3)}$ are presented in this paper. No IR spectrum of the nitro group coordinated to porphyrinatocobalt(III) has been shown previously though some IR spectra of the nitro groups coordinated to Co(III) ions have been reported for hexanitrocobaltate(III)$^{4,5)}$ and some nitroamminecobalt(III) complexes.$^{5-7)}$

Compound **1** is obtained from [Co^{II}(tpp)(NO)], piperidine and O$_2$ gas at a pressure of 1 atm in 1,2-dichloroethane. The crude **1** is recrystallized from a mixture of dichloromethane and methyl alcohol. Nitro(5,10,15,20-tetraphenylporphyrinato)(pyridine)cobalt(III) ([Co^{III}(tpp)(py)(NO$_2$)], (**2**)) was also prepared in the similar way for the comparison of the IR

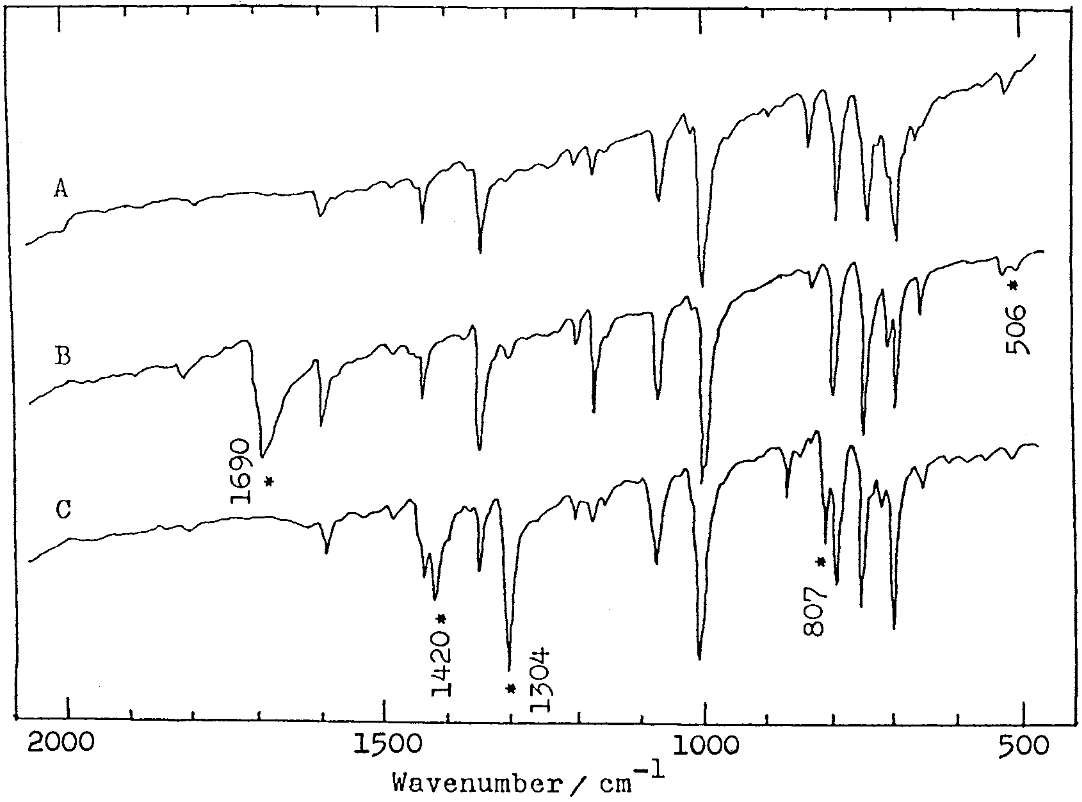

Fig. 1. IR spectra of porphyrinatocobalt complexes (KBr pellets). (A) [Co^{II}(tpp)]; (B) [Co^{II}(tpp)(NO)]; (C) [Co^{III}(tpp)(pip)(NO$_2$)]. Bands marked with (*) are due to the nitrosyl and nitro groups.

spectra of **1** and **2**. The IR spectra were recorded on a JASCO DS-701G spectrometer in the range of 2000-500 cm^{-1} at room temperature using KBr pellets.

The IR spectra of [Co^{II}(tpp)(NO)] and **1** are shown in Fig. 1. The band at 1690 cm^{-1} (1689 cm^{-1} in Ref. 1 or 1690 cm^{-1} in Ref. 8) due to the nitrosyl group in [Co^{II}(tpp)(NO)] (Fig. 1B) disappeared completely and three new bands appeared at 1420, 1304 and 807 cm^{-1} in the spectrum of **1** (Fig. 1C). These three bands can be assigned, respectively, as the asymmetric stretching, symmetric stretching and deformation vibrations [ν_{as}, ν_s, and δ (cm^{-1})] of the nitro group coordinated to the porphyrinatocobalt(III) according to the literatures.$^{5-7)}$ The IR spectrum of **2** was mostly similar to that of **1** except for that the weak bands at 869 and 848 cm^{-1} were not seen and the δ band was not so sharp as in **1**. The previous

Table 1. IR data of some cobalt(III) nitro complexes

Complex	ν_{as} / cm^{-1}	ν_s / cm^{-1}	δ / cm^{-1}	Reference
$Na_3[Co(NO_2)_6]$	1471-1408	1333	847,833	4
$K_3[Co(NO_2)_6]$	1396,1381	1332	834	5
$[Co(NH_3)_5NO_2]Cl_2$	1430	1315	825	6
	1426	1313	824	7
	1428	1310	824	5
$[Co(tpp)(pip)(NO_2)]$	1420	1304	807	this work
$[Co(tpp)(py)(NO_2)]$	1425	1306	812	this work

assignments of the ν_{as} and ν_s bands (**1** = 1304, 1200 cm^{-1}; **2** = 1306, 1210 cm^{-1})[9] are renewed. Some IR data of the nitro cobalt compounds are shown in Table 1.

The comparison of the ν_{as} bands for **1** (1420 cm^{-1}) and for **2** (1425 cm^{-1}) shows that the frequency is lower in **1** than in **2**. While the frequencies of the ν_s bands for **1** (1304 cm^{-1}) and for **2** (1306 cm^{-1}) are not appreciably different. Therefore the separation between the frequencies of the ν_{as} and ν_s bands is slightly smaller for **1** (116 cm^{-1}) than for **2** (119 cm^{-1}). As it is pointed out that the separation increases as the metal-NO_2 bond becomes stronger,[5] the Co-NO_2 bond seems to be weaker in **1** (1.897(11) Å)[10] than in **2** though the difference may be small. The ν_{as} band of **1** could be observed as a sharp band probably because it was shifted towards lower frequencies due to that the Co-NO_2 bond in **1** is weaker while the ν_{as} band of **2** was observed as a shoulder on the band at 1439 cm^{-1} due to the porphyrin ring.

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