Infrared Spectrum of Nitro(5,10,15,20-tetraphenylporphyrinato)(4-methylpyridine)cobalt(III)

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IR spectrum of the title compound is measured in the 500 to 300 cm^{-1} region. The band at 346 cm^{-1} is shifted depending on the fifth ligand (L) and assigned to the skeletal deformation vibration band coupled with the Co–NO$_2$ stretching and Co–L stretching vibration bands.

Nitrosyl(5,10,15,20-tetraphenylporphyrinato)cobalt(II) ([Co^{II}(tpp)(NO)])[1] reacts with molecular oxygen in the presence of 4-methylpyridine (4-Mepy) to give nitro(5,10,15,20-tetraphenylporphyrinato)(4-methylpyridine)-cobalt(III) ([Co^{III}(tpp)-(4-Mepy)(NO$_2$)], (**1**)).[2] Previously we reported the IR spectrum of [Co^{III}(tpp)(pip)(NO$_2$)] (pip: piperidine) and band assignments of the nitro group in the range of 2000 to 500 cm^{-1}.[3] There, the asymmetric stretching, symmetric stretching, and deformation vibrations of the nitro group [ν_{as}, ν_s, and δ (cm^{-1})] were assigned. These bands for (C$_2$H$_5$OH)Co(TPP)(NO$_2$)[4] and Fe(TPP)(NO$_2$)(1-MeIm)[5] are shown mainly in the 1800–800 cm^{-1} region, and the spectra under 800 cm^{-1} are not shown. In this paper the IR spectra in the lower frequency region (500–300 cm^{-1}) and the band assignments of the nitro group in **1** are presented.[6] The purpose of this work is to assign the Co–NO$_2$ stretching band.

Compound **1** is obtained from [Co^{II}(tpp)(NO)], 4-Mepy, and O$_2$ gas at a pressure of 1 atm in 1,2-dichloroethane. After the evaporation of solvent the crude **1** is recrystallized from a mixture of dichloromethane and methyl alcohol. The IR spectra were recorded on a JASCO DS-701G spectrometer in the range of 500–300 cm^{-1} at room temperature using KBr pellets.

The IR spectra of [Co^{II}(tpp)(NO)] and **1** are shown in Figure 1. The band at 506 cm^{-1} due to the nitrosyl group in [Co^{II}(tpp)(NO)] (Figure 1a) disappeared completely, and five new bands appeared at 496, 360, 346, 332, and 316 cm^{-1} for **1** under 500 cm^{-1}. The assignments of these five bands are described below.

The IR spectrum of free (noncoordinated) 4-Mepy is shown in Figure 2.[7] There are two strong absorptions at 510 and 481 cm^{-1}. As the average value of the two frequencies is 496 cm^{-1}, band 1 is attributable to the absorptions due to the fifth ligand (L), 4-Mepy. The IR absorptions by L were scarcely observed when L were piperidine (pip) and pyridine (py). But when L is 4-Mepy the absorptions around 496 cm^{-1} are very strong and the absorptions of L may appear.

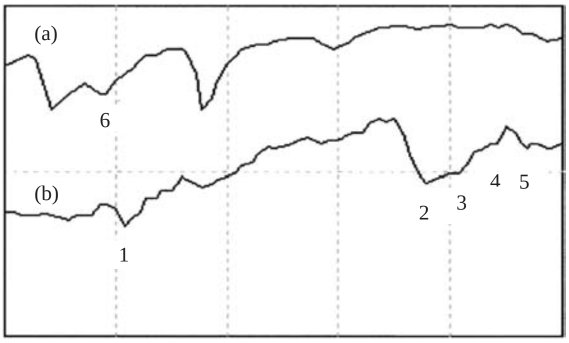

Figure 1. IR spectra: (a) [Co(tpp)(NO)], 6: 506 cm^{-1}; (b) **1**, 1: 496; 2: 360; 3: 346; 4: 332; 5: 316 cm^{-1}.

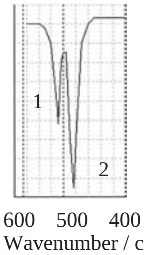

Figure 2. IR spectrum of 4-methylpyridine: 1, 510; 2, 481 cm^{-1}.[7]

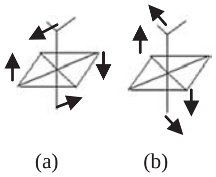
(a) (b)

Figure 3. Out of plane skeletal deformation modes.

The IR spectrum of the analogous [Co(NO$_2$)(NH$_3$)$_5$]$^{2+}$ ion (**2**) has already been reported, and the band appearing at 361 cm^{-1} was assigned to the skeletal deformation bands as shown in Figures 3a and 3b.[8] Band 2 at 360 cm^{-1} in **1** also seems to be due to the same skeletal deformation bands as shown in **2**. But the absorption frequencies of band 2 were scarcely affected by L and the rocking mode vibration of the nitro group also appeared at 361 cm^{-1} in **2**; the possibility is not denied that band 2 is also due to the rocking mode vibration in **1**. If band 2 is attributed to the skeletal deformations as shown in Figure 3, the absorption frequencies may change depending on L. Thus it cannot be denied that band 2 is the overlapped bands of the rocking and skeletal deformation mode vibrations as in the case of **2**.

Band 3 at 346 cm^{-1} is shifted to higher frequencies when L is py as is shown in Figure 4. In the case of **2** it was described that some vibrations may be coupled together and reveal several bands in the region 400–250 cm^{-1}.[8] Similarly it may be often difficult to assign one band to a pure vibration mode in the region 400–250 cm^{-1} in **1**. The absorption position (346 cm^{-1}) and the shift by L indicate that band 3 may be assigned to the skeletal deformation mode vibration (ν_{12}[8]) as is shown in Figure 5b corresponding to the band at 335 cm^{-1} in **2** and probably coupled with other vibrations, ν_{10} and ν_{13}[8] which are shown in Figures 5a and 5c.

Bands 4 and 5 shift from 332 and 316 to 337 and 324 cm^{-1} as is shown in Figure 4 and Table 1 when L is changed from 4-Mepy to py. These higher frequency shifts are the same as that of

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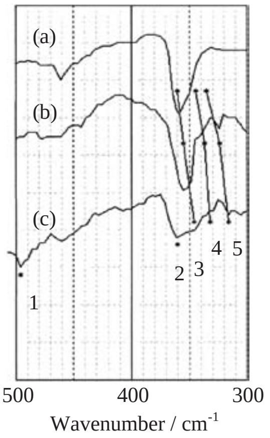

Figure 4. IR spectra of [Co(tpp)(L)(NO$_2$)]: (a) L = pip, (b) L = py, (c) L = 4-Mepy.

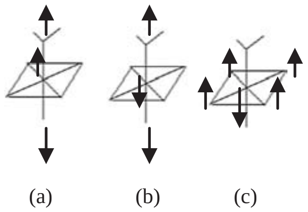

Figure 5. Out of plane skeletal deformation modes.

Table 1. Some IR bands concern with metal–NO$_2$ stretching vibrations

Complex	Band 3 /cm^{-1}	Band 4 /cm^{-1}	Band 5 /cm^{-1}	ref
[Co(tpp)(pip)(NO$_2$)]	360	344	335	t. w.[a]
[Co(tpp)(py)(NO$_2$)]	355	337	324	t. w.
[Co(tpp)(4-Mepy)(NO$_2$)]	346	332	316	t. w.
[Co(NO$_2$)(NH$_3$)$_5$]$^{2+}$	335	(290)	482	8

[a] t. w. represents this work.

band 3. Thus bands 3, 4, and 5 may appear to be coupling with each other. As band 3 is assigned to ν_{12} (the skeletal deformation vibration) as described above, bands 4 and 5 can be assigned to ν_{13} and ν_{10} (approximately the Co–NO$_2$ stretching and Co–L stretching vibrations), respectively. But it is difficult to decide which one of the bands 4 or 5 corresponds to ν_{13} or ν_{10}. Some speculation is shown below that band 4 and band 5 are assigned to ν_{13} and ν_{10}. Band 4 shifts by 12 cm^{-1} and band 5 shifts by 19 cm^{-1} when L is changed from 4-Mepy to pip. The shift of band 4 is smaller than that of band 5. The vibration modes of ν_{13} and ν_{10} (Figure 5) show that though ν_{10} is affected by L directly, ν_{13} is not affected by L directly. So the effect of L may be smaller in band 4 than in band 5. Thus band 4 is assigned to ν_{13} and band 5 is assigned to ν_{10} for the time being.

The IR spectra of [Co(tpp)(L)(NO$_2$)] complexes are shown together with that of **2** to compare the spectra in Figure 6. It shows that the couplings of the three bands (bands 3, 4, and 5) are characteristically remarkable for [Co(tpp)(L)(NO$_2$)] complexes.

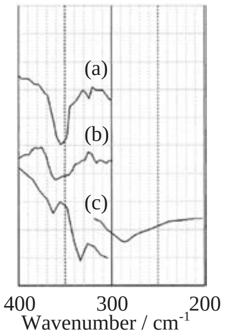

Figure 6. IR spectra of [Co(tpp)(L)(NO$_2$)]: (a) L = py, (b) L = 4-Mepy, (c) **2**.[8]

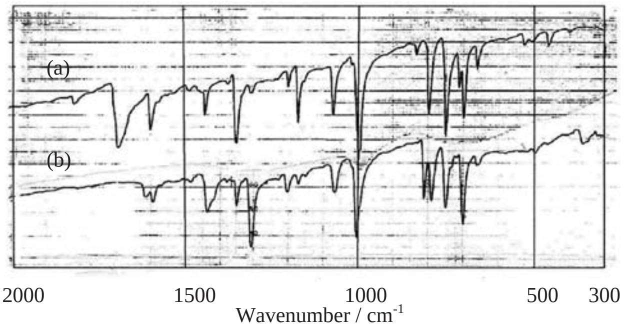

Figure 7. IR spectra of nitrosyl and nitro complexes of porphyrinatocobalt (KBr pellets), (a) [Co(tpp)(NO)]; (b) **1**.

The IR spectra in the range of 2000–300 cm^{-1} are also shown to view the wide range of spectra for some representative [Co(tpp)(NO)] and [Co(tpp)(4-Mepy)(NO$_2$)] complexes in Figure 7. It should be noted that the intensities of the bands in the lower frequencies are very weak compared to that at the high frequencies, and it seems more difficult to assign the spectra precisely in the lower frequencies region. Some metal–NO$_2$ stretching IR bands are reported for various complexes, for example, K$_3$[Co(NO$_2$)$_6$] (418 cm^{-1}), Na$_3$[Co(NO$_2$)$_6$] (451 and 373 cm^{-1}),[9] and recently for (*i*Pr-TIC)Cu(NO$_2$) (393 cm^{-1}),[10] but the absorption positions are considerably different for each complex. The apparent couplings among the three bands in [Co(tpp)(L)(NO$_2$)] complexes as described above seem to be characteristic for [Co(tpp)(L)(NO$_2$)] complexes.

References and Notes

† The experiments of this work were carried out at Faculty of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033 (between Jan., 1981-July, 1985); Present address: 1-15-2 Fujimoto, Kokubunji, Tokyo 185-0031

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