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## Infrared Absorption Spectra of Aminobenzoic Acid Coordination Compounds

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Several divalent metal-aminobenzoic acid coordination compounds were prepared in aqueous solutions and their thermal analyses, magnetic moments, and infrared spectra were investigated. These coordination compounds have the structure of  $ML_2$  or  $ML_2 \cdot nH_2O$  and are coordinated with amino and carboxyl groups of the ligand. Metal-*o*-aminobenzoic acid chelates give approximately the same infrared spectra but metal-*m*- and *p*-aminobenzoic acid coordination compounds are classified into two groups by their infrared spectra. Detailed assignments for the infrared absorption bands of the metal-coordination compounds have been made by a comparison of the spectra with those of the ligand and its related compounds.

The infrared spectra of aliphatic  $\alpha$ -amino acid chelates have been investigated in great numbers but not those of metal aromatic amino acid coordination compounds. Hill and Curran<sup>1)</sup> prepared several divalent metal-*o*-aminobenzoic acid coordination compounds in aqueous solutions, and showed them to have a *trans* square-planar configuration from their ultraviolet spectra and infrared spectra at about  $3200\text{ cm}^{-1}$ .

Several stability constants of metal-*o*-aminobenzoic acid coordination compounds have been reported.<sup>2,3)</sup> Decker and Frye<sup>4,5)</sup> measured the infrared spectra of

metal *N*- and ring-substituted *o*-aminobenzoic acid coordination compounds and studied the substituent effect on stability constants. They also prepared<sup>6)</sup> metal coordination compounds of aminoterephthalic acid and 3-aminophthalic acid and indicated that the compounds have a dimer structure and nitrogen and oxygen are coordinated to the metal cations. In the former two carboxyl groups and one amino group are coordinated to each metal, but in the latter two amino groups and one carboxyl group are coordinated to one metal and three carboxyl groups to the other metal. Alyariya *et al.*<sup>7)</sup> studied the infrared spectra of *o*-, *m*-, and *p*-aminobenzoic acid cadmium(II) coordination compounds and indicated that nitrogen and oxygen are coordinated to cadmium(II) in *o*-isomer but only

1) A. G. Hill and C. Curran, *J. Phys. Chem.*, **64**, 1529 (1960).

2) W. F. Harris and T. R. Sweet, *ibid.*, **60**, 509 (1956).

3) W. F. Harris and T. R. Sweet, *J. Amer. Chem. Soc.*, **77**, 2893 (1955).

4) J. S. Decker and H. Frye, *Z. Naturforschug*, **21b**, 527 (1966).

5) J. S. Decker and H. Frey, *ibid.*, **21b**, 522 (1966).

6) J. S. Decker and H. Frye, *ibid.*, **21b**, 626 (1966).

7) M. K. Alyariya, T. Saidaliev, and Y. T. Tashpulatov, *Zh. Neorgan. Khim.*, **10**, 1493 (1965).

nitrogen is coordinated in *m*- and *p*-isomer. Aggarwal and Singh<sup>8)</sup> prepared the tin(IV) coordination compounds of three isomers in many organic solvents and showed that coordination occurs through nitrogen only. Khakimow and Azizov<sup>9)</sup> indicated that cobalt (II) coordination compounds of three isomers had the following molecular formulas.  $[(o\text{-C}_7\text{H}_6\text{NO}_2)_2\text{Co}]$ ,  $[(m\text{-C}_7\text{H}_6\text{NO}_2)_2\text{Co}]\text{H}_2\text{O}$ ,  $[(p\text{-C}_7\text{H}_6\text{NO}_2)_2\text{Co}]\cdot 4\text{H}_2\text{O}$ .

In this investigation, the infrared spectra of several divalent metal coordination compounds of the three isomers of aminobenzoic acid have been studied in the region 4000—200  $\text{cm}^{-1}$  and detailed assignments for the observed bands have been made.

## Experimental

**Preparation of compounds.** Bis(*o*-, *m*-, *p*-aminobenzoato) copper(II), zinc(II), nickel(II), cobalt(II), and cadmium(II) were prepared as follows. To a solution of 0.2 mol of aminobenzoic acid and 0.2 mol of sodium hydroxide dissolved in 200 ml of water was added 0.1 mol of metal chloride with stirring. The solution was heated to 80 °C and stirred for two days in the case of bis(*p*-aminobenzoato)-nickel, cobalt, zinc, and cadmium and for half an hour for all the other compounds.

Bis(*o*-aminobenzoato)-palladium (II) and bis(*m*-aminobenzoato)-palladium (II) were prepared by the same method as above but at room temperature. The resulting precipitate was filtered and washed several times with hot water and then with dioxane and was dried at 100 °C *in vacuo* for several hours.

*o*-Aminobenzoic acid chelates, Found: C, 49.96; H, 3.47; N, 8.42%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Cu}$ : C, 50.07; H, 3.60; N, 8.34%. Found: C, 49.60; H, 3.84; N, 8.28%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Zn}$ : C, 49.80; H, 3.58; N, 8.30%. Found: C, 43.50; H, 3.22; N, 7.25%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Cd}$ : C, 43.71; H, 3.14; N, 7.28%. Found: C, 50.90; H, 3.68; N, 8.21%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Ni}$ : C, 50.81; H, 3.65; N, 8.46%. Found: C, 50.82; H, 3.61; N, 8.55%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Co}$ : C, 50.77; H, 3.65; N, 8.46%. Found: C, 44.45; H, 3.42; N, 7.46%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Pd}$ : C, 44.41; H, 3.19; N, 7.40%.

*m*-Aminobenzoic acid coordination compounds, Found: C, 50.04; H, 3.48; N, 8.50%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Cu}$ : C, 50.07; H, 3.60; N, 8.34%. Found: C, 48.38; H, 3.25; N, 8.07%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Zn}\cdot 1/2\text{H}_2\text{O}$ : C, 48.51; H, 3.77; N, 8.10%. Found: C, 43.71; H, 3.26; N, 7.18%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Cd}$ : C, 43.71; H, 3.14; N, 7.28%. Found: C, 45.44; H, 4.22; N, 7.74%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Ni}\cdot 2\text{H}_2\text{O}$ : C, 45.82; H, 4.38; N, 7.63%. Found: C, 50.82; H, 3.61; N, 8.55%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Co}$ : C, 50.77; H, 3.65; N, 8.46%. Found: C, 40.53; H, 3.95; N, 7.06%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Pd}\cdot 2\text{H}_2\text{O}$ : C, 40.55; H, 3.88; N, 6.75%.

*p*-Aminobenzoic acid coordination compounds, Found: C, 50.04; H, 3.28; N, 8.13%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Cu}$ : C, 50.07; H, 3.60; N, 8.34%. Found: C, 38.17; H, 3.90; N, 6.45%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Cd}\cdot 3\text{H}_2\text{O}$ : C, 38.30; H, 4.14; N, 6.38%. Found: C, 46.01; H, 4.47; N, 7.78%. Calcd for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Ni}\cdot 2\text{H}_2\text{O}$ : C, 45.82; H, 4.38; N, 7.63%. Found: C, 43.75; H, 3.76; N, 7.57%. Calcd

for  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{Pd}\cdot 1/2\text{H}_2\text{O}$ : C, 43.37; H, 3.38; N, 7.22%.

**Deuteration of Compounds.** The *N*-deuterated metal coordination compounds were prepared according to the same procedures as mentioned above in 99.7% deuterium oxide solution.

**Absorption Measurements.** The infrared spectra from 4000 to 200  $\text{cm}^{-1}$  were recorded on Leitz 221, Hitachi EPI-G<sub>2</sub> and Hitachi EPI-L infrared spectrophotometers and were calibrated with polystyrene, 1,2,4-trichlorobenzene, carbon dioxide and water vapour. Samples were prepared as potassium bromide discs in the region 4000—700  $\text{cm}^{-1}$  and nujol mulls in the region 700—200  $\text{cm}^{-1}$ . All spectra were checked using nujol mulls.

**Thermal Analysis.** Thermal analysis was carried out with Rigaku Denki D. T. A. 8001 from room temperature to 400 °C in air, the decrease in weight being measured when an endothermic reaction occurred. The results coincided with those of elemental analyses.

**Magnetic Moment.** Magnetic susceptibility measurements were carried out on finely divided powdered samples using the conventional Gouy method. All determinations were made at room temperature (20 °C). The cell constants were obtained using  $\text{Hg}(\text{CoSCN})_4$  as a standard. The magnetic moments were calculated by the formula  $\mu_{\text{eff}} = \sqrt{2.83\chi}$ .

## Results and Discussion

***o*-Aminobenzoic Acid Chelates.** The infrared spectra of the copper(II) and cobalt(II) chelates and ligand are shown in Fig. 1. The infrared spectra of all other chelates are similar to those of copper(II) or cobalt(II) in the region 4000—500  $\text{cm}^{-1}$ . In the case of copper(II) chelates, two peaks at 3234 and 3135  $\text{cm}^{-1}$  shifted to 2432 and 2294  $\text{cm}^{-1}$  on *N*-deuteration are about 300  $\text{cm}^{-1}$  lower than those of ligand and ligand sodium salt and are assigned to  $\text{NH}_2$  stretching vibrations of the coordinated  $\text{NH}_2$  groups. The carboxylate stretching vibrations are assigned to the two bands at 1551 and 1384  $\text{cm}^{-1}$ , since the observed bands in the region 1350—1660  $\text{cm}^{-1}$  not disappearing on *N*-deuteration are  $\text{COO}^-$  and  $\text{C}=\text{C}$  stretching vibrations, and two peaks at 1551 and 1384  $\text{cm}^{-1}$  are shifted with the variation of metals as shown in Table 1.

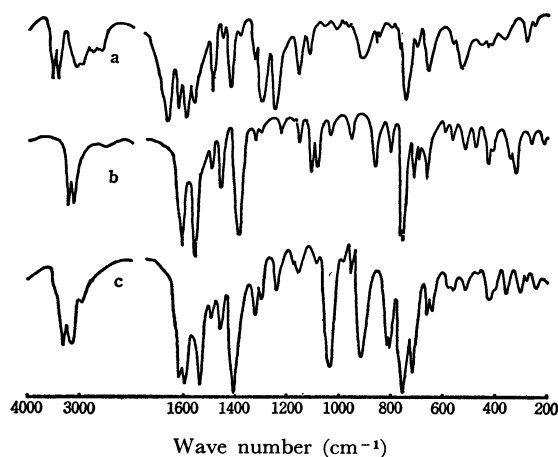


Fig. 1. Infrared absorption spectra of *o*-aminobenzoic acid and its chelates in KBr discs.

(a): *o*-aminobenzoic acid, (b): Cu(II), (c): Co(II)

8) R. C. Aggarwal and P. P. Singh, *J. Inorg. Nucl. Chem.*, **27**, 2593 (1965).

9) K. Khakimow and H. Azizov, *Trudy Tashkent Farm. Inst.*, **2**, 279 (1960).

TABLE 1. OBSERVED FREQUENCIES AND ASSIGNMENTS FOR METAL-*o*-AMINOBENZOIC ACID CHELATES (cm<sup>-1</sup>)

Cd(II)	Ni(II)	Co(II)	Zn(II)	Cu(II)	Pd(II)	Assignments
3287 m	3298 s	3306 m	3294 m	3234 m	3165 s	NH <sub>2</sub> asym. str.
3137 m	3125 s	3138 m	3127 m	3135 m	3090 m	NH <sub>2</sub> sym. str.
1616 m	1614 s	1615 s	1614 s	1604 s	1620 s	C=C str.
1591 s	1592 s	1591 s	1592 s		1607 s	C=C str.
1534 vs	1545 vs	1535 vs	1542 s	1551 s	1555 m	COO <sup>-</sup> asym. str.
1493 sh	1493 m	1493 w	1490 w	1491 w	1491 w	C=C str.
1457 m	1458 s	1458 m	1457 m	1459 m	1451 m	C=C str.
1404 vs	1410 vs	1409 vs	1407 vs	1384 s	1358 s	COO <sup>-</sup> sym. str.
1327 w	1330 m	1326 m	1327 w	1327 w		
1300 w	1300 w	1300 w	1299 w	1301 vw	1303 w	
1237 w	1242 w	1241 w	1239 w	1231 w	1212 vw	C-N str.
	1178 vw	1178 vw	1175 vw	1177 vw	1194 vw	
1154 w	1154 w	1152 w	1152 w	1154 w	1157 w	
1082 w	1096 m	1087 w	1091 w	1085 w	1088 w	CH in plane def.
1024 m	1067 m	1035 s	1047 s	1108 m		NH <sub>2</sub> wagging
1002 m						
	1041 w			1037 w	1043 w	
	984 vw	983 vw	983 vw			
951 w	952 w	951 w	952 w	953 w	950 w	CH out of plane def.
864 m	869 s	868 m	868 m	866 m	882 m	
839 vw						
809 m	815 m	813 m	811 m	812 m	819 w	
801 m	809 m	807 m	808 m	807 m	803 w	COO <sup>-</sup> scissors
754 s	753 vs	753 vs	753 s	756 s	742 s	CH out of plane def.
716 m	717 s	717 s	716 s	715 m	701 m	benzene ring def.
705 vw						
654 m	660 s	669 m	667 sh	669 m	668 m	benzene ring def.
668 sh	672 sh	645 u	650 u	698 m		NH <sub>2</sub> rocking
582 vw	589 w	585 w	586 w	590 vw	584 vw	benzene ring def.
559 vw	567 w	562 w	558 w	567 vw	535 w	COO <sup>-</sup> wagging
516 w	519 m	516 m	515 w	516 w		
459 vw	474 m	466 vw	461 vw	478 w	481 m	COO <sup>-</sup> rocking
407 m	426 w	419 m	416 m	412 m	400 m	benzene ring def.
400 sh	413 sh	410 sh				CN def.
333 w	312 w	300 m	405 sh	422 w	442 m	M-N str.
	365 m	355 m	347 w	342 w	345 w	CC def.
			290 w	328 w	335 w	
		280 vw	282 w			
270 w	261 w	245 w	248 w	266 w	273 w	CN def.
				210 w	222 w	M-O str.

Abbreviation: s=strong, m=medium, w=weak, sh=shoulder

The remaining bands can thus be assigned to C=C stretching vibrations.

The infrared spectra of copper(II) and palladium(II) chelates of *o*-aminobenzoic acid differ slightly from those of other metal chelates. However, the difference is not so great as in the case of *m*- and *p*-aminobenzoic acid coordination compounds. Curran and Hill reported that copper(II) chelate of *o*-aminobenzoic acid has a *trans* square planar configuration. The magnetic moment of nickel(II) chelate is 3.22 B.M. which shows that it has no *trans* square planar configuration. Nyholm<sup>10)</sup> reported that the magnetic

moments of nickel(II) chelates of various ligands having an octahedral configuration are 3.1–3.6 B.M.. Thus, from the similarity of their infrared spectra, we may assume that copper(II) and palladium(II) chelates have a *trans* square planar configuration and the other metal chelates an octahedral configuration. Since the sodium chloride region spectra of all chelates are approximately similar, absorption bands except for vibrations related with metal-ligand bonds should be observed at approximately the same position also in the far infrared region. Since the frequency shifts of carboxylate stretching vibrations by the difference of metals are smaller than those of amino stretching vibrations and in aliphatic  $\alpha$ -amino acid metal

10) R. S. Nyholm, *Record Chem. Progr.*, **19**, 45 (1958).

chelates,<sup>11,12</sup> the metal-nitrogen and metal-oxygen stretching vibrations are observed in the region 450—300  $\text{cm}^{-1}$  and 300—180  $\text{cm}^{-1}$ , respectively. Thus the most metal sensitive band at about 380  $\text{cm}^{-1}$  which is not observed in the ligand and ligand sodium salt<sup>13</sup> is reasonably assigned to metal-nitrogen stretching vibration and the bands at 222  $\text{cm}^{-1}$  for palladium(II) and 210  $\text{cm}^{-1}$  for copper(II) are assigned to metal-oxygen stretching vibration.

Detailed assignments were made by a comparison of the spectra of ligand, ligand sodium salt<sup>13</sup>, *o*-chlorobenzoic acid,<sup>14</sup> *o*-chloroaniline,<sup>15</sup> and *o*-dichlorobenzene.<sup>16</sup> The results are shown in Table 1.

*m*-Aminobenzoic Acid Coordination Compounds. The infrared spectra of the copper(II) and cobalt(II) coordination compounds and ligand are shown in Fig. 2.

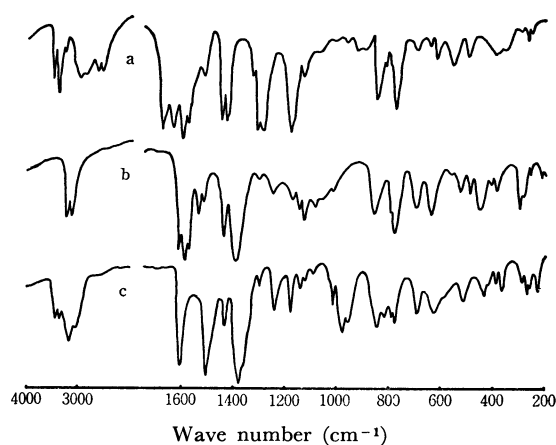


Fig. 2. Infrared absorption spectra of *m*-aminobenzoic acid and its coordination compounds in KBr discs.  
(a): *m*-aminobenzoic acid, (b): Cu(II), (c): Co(II)

In the region 3400—2800  $\text{cm}^{-1}$ , the important frequencies are those due to  $\text{NH}_2$  stretching vibrations in the metal coordination compounds. Two peaks at 3255 and 3147  $\text{cm}^{-1}$  in the copper(II) coordination compound are shifted on *N*-deuteration to 2428 and 2298  $\text{cm}^{-1}$ , respectively, and the ratios ( $\nu_{\text{NH}_2}/\nu_{\text{ND}_2}$ ) between  $\text{NH}_2$  and  $\text{ND}_2$  stretching vibrational frequencies of these two bands are 1.34 and 1.37, respectively, being similar to those of aliphatic  $\alpha$ -amino acid chelates.<sup>11,12</sup> The two peaks are observed at frequencies lower than those of *m*-aminobenzoic acid sodium salt<sup>13</sup> by about 180—200  $\text{cm}^{-1}$ , and are assigned to  $\text{NH}_2$  stretching vibrations of the coordinated  $\text{NH}_2$  groups. In the region 600—270  $\text{cm}^{-1}$ , the spectra contain a new band at 382  $\text{cm}^{-1}$  in addition to the vibrations

in the spectra of ligand. The frequencies of  $\text{NH}_2$  and  $\text{COO}^-$  stretching vibrations in the metal *m*-aminobenzoic acid coordination compounds are observed in approximately the same region as in *o*-isomer chelates, the frequency shifts due to the different metals being also approximately the same as in *o*-isomer chelates. Thus, it is reasonable to assign this band to the metal-nitrogen stretching vibration. The ligand can be assumed to be coordinated to copper through the nitrogen atom. The frequency shifts of the  $\text{COO}^-$  stretching vibrations on coordination in the copper(II) coordination compound are smaller than those of  $\text{NH}_2$  stretching vibration. However, it can hardly be said that the carboxyl group is not coordinated to the metal and remains as a carboxylic acid as Alyariya *et al.*<sup>7</sup> reported with the cadmium coordination compound,<sup>7</sup> since OH and C=O stretching vibrations, the combination bands of OH in plane deformation and C—O stretching vibration are not observed in copper(II) *m*-aminobenzoic acid coordination compound (Fig. 2 and Table 2.). This is also inconsistent with the result of elemental analysis which excludes the existence of the carboxyl group as a sodium salt. A new band is observed at 223  $\text{cm}^{-1}$  which is not present in the ligand. This band is assigned to the metal-oxygen stretching vibration by considering the results of metal *o*-aminobenzoic acid chelates and aliphatic  $\alpha$ -amino acid chelates.<sup>11,12</sup> It is therefore concluded that the oxygen of the carboxyl group is also coordinated to copper atom. Similar conclusions can be drawn for the palladium(II) and Zinc(II) coordination compounds from the similarity of their infrared spectra to that of the copper(II) coordination compound as shown in Table 2.

The infrared spectrum of cobalt(II) coordination compound is shown in Fig. 2. This differs somewhat from that of the copper(II) coordination compound. In the region 1300—1650  $\text{cm}^{-1}$  only four peaks are observed in cobalt(II) but seven in copper(II). In cobalt(II) the strong bands at 1006 and 989  $\text{cm}^{-1}$  are observed instead of the strong bands around 1110  $\text{cm}^{-1}$  in copper(II). In the region 600—800  $\text{cm}^{-1}$  the number of bands are the same but their shapes differ. Nevertheless, these spectra indicate that the coordination to metal has occurred through both nitrogen and oxygen in the cobalt(II) coordination compound for the same reasons mentioned above.

The spectrum of cadmium(II) coordination compound is similar to that of cobalt(II). Though the nickel(II) coordination compound has two molecules of water as thermal and elemental analyses show, the spectrum of the nickel(II) dihydrate is also similar to that of cobalt(II). It is therefore concluded that the six metal coordination compounds of *m*-aminobenzoic acid have a coordination of both nitrogen and oxygen with metal. The result is inconsistent with that of Alyariya *et al.*<sup>7</sup> in which only nitrogen is coordinated to cadmium(II).

In the case of aliphatic  $\alpha$ -amino acids chelates, the antisymmetric carboxylate stretching frequency increases and symmetric frequency decreases in comparison with those of ligand and ligand sodium salt,

11) J. F. Jackovitz and J. L. Walter, *Spectrochim. Acta*, **22**, 1393 (1966).

12) J. F. Jackovitz, J. A. Durkin and J. L. Walter, *ibid.*, **23A**, 67 (1967).

13) T. Inomata and T. Moriwaki, *Nippon Kagaku Zasshi*, **91**, 819 (1970).

14) E. Spinner, *J. Chem. Soc.*, **B**, 1967, 874.

15) V. B. Singh, R. N. Singh, and I. S. Singh, *Spectrochim. Acta*, **22**, 927 (1966).

16) P. R. Griffiths and H. W. Thompson, *Proc. Roy. Soc., Ser. A*, **298**, 51 (1967); H. F. Shurvell, B. Dulaurens, and P. Pestel, *Spectrochim. Acta*, **22**, 333 (1966).

TABLE 2. OBSERVED FREQUENCIES AND ASSIGNMENTS FOR METAL-*m*-AMINOBENZOIC ACID COORDINATION COMPOUNDS

Pd(II)	Cu(II)	Zn(II)	Ni(II)	Cd(II)	Co(II)	Assignments
3191 m	3255 m	3276 m	3348 m	3350 m	3356 m	NH <sub>2</sub> asym. str.
3093 m	3147 m	3240 m	3264 m	3270 m	3287 m	NH <sub>2</sub> sym. str.
		3105 w	3164 m			
			3059 m			
1620 s	1629 s	1632 s	1608 m	1588 m	1587 m	C=C str.
		1550 w		1608 w		NH <sub>2</sub> scissors
1582 vs	1572 vs	1569 vs	1542 vs	1541 vs	1538 vs	COO <sup>-</sup> asym. str.
	1531 m					
1494 w	1495 w	1501 w				
1455 s	1459 m	1464 s	1453 s	1458 s	1454 m	C=C str.
1348 vs	1406 vs	1400 vs	1394 vs	1391 vs	1391 vs	COO <sup>-</sup> sym. str.
	1386 vs					
1314 w	1325 w	1326 w	1316 w	1313 w	1323 w	
1298 w	1303 w	1305 w	1305 w	1301 w	1303 w	
1220 w	1240 w	1241 w	1244 m	1248 m	1242 m	CN str.
	1187 vw	1199 w				
1160 m	1153 m	1165 m				NH <sub>2</sub> wagging
1132 m	1128 m	1136 m				
1110 m	1106 m	1107 m		1119 w	1119 w	CH in plane def.
1074 m	1073 m	1076 m	1079 w	1074 w	1074 w	
1001 w	1001 w	1001 w	1152 w	1168 w	1163 w	
			1011 s	1007 s	1006 s	NH <sub>2</sub> wagging
			995 vs	988 vs	989 vs	
		933 m				
929 m	927 m	924 m	926 m	924 m	925 m	CH out of plane def.
886 m	889 m	877 m				
				917 m	914 m	
				902 m	903 m	
			883 m	902 m	896 m	
			818 w	825 w	822 w	
807 s	802 s	808 s	783 s	785 s	787 s	COO <sup>-</sup> scissors
796 m	786 s	789 m				
758 s	759 s	760 s	769 vs	775 vs	776 vs	CH out of plane def.
				688 m	690 m	
678 s	677 s	677 s	683 m	683 m	683 m	COO <sup>-</sup> wagging
670 m	668 sh	669 m	672 m	667 m	669 m	C=C def.
619 w	592 w	564 w				
			568 s	586 s	597 m	NH <sub>2</sub> rocking
			584 vs	561 vs	575 m	C=C def.
556 m	545 w	540 m	547 s	548 s	551 m	C=C def.
572 m	528 w	520 m	526 m	516 m	523 w	COO <sup>-</sup> rocking
446 m	458 m	446 m	435 w	433 w	440 w	C=C def.
423 w	425 w	413 w	400 m	413 m	417 m	CN def.
391 w	387 w	370 w				C-C def.
			380 m	368 m	382 m	
470 sh	437 w	429 sh	350 w	360 w	369 m	MN str.
293 w	280 w		268 w		268 m	CN def.
271 w	244 m	252 w	245 w	243 w	250 m	C-C def.
227 w	223 w	209 w				MO str.

Abbreviations: s=strong, m=medium, w=weak, sh=shoulder

Rosenberg<sup>17)</sup> showed that the nickel-oxygen bond is essentially ionic, and the frequencies of carboxylate stretching vibration are the same as those of an amino acid sodium salt. In the case of *m*-aminobenzoic

acid, palladium(II), copper(II), and zinc(II) coordination compounds have a similar tendency but for nickel(II), cobalt(II), and cadmium(II) the frequencies of antisymmetric and symmetric carboxylate stretching vibrations shift to lower frequencies in comparison with those of the sodium salt<sup>13)</sup> and the positions are

17) A. Rosenberg, *Acta. Chem. Scand.*, **10**, 840 (1956).

nearly the same for these compounds. This leads to conclusion that when the carboxyl group is coordinated to palladium(II), copper(II), and zinc(II) they have the structure  $-C\begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}-M$ , and nickel(II), cobalt(II), and cadmium(II) derivatives can be represented as the structure  $-C\begin{smallmatrix} \diagup O \\ \diagdown O \end{smallmatrix}-M$ .

These coordination compounds can be divided into two groups which shows that each group has the same configuration. The magnetic moments of copper(II) (2.02 B.M.), cobalt(II) (5.08 B.M.), and nickel(II) (3.12 B.M.) indicate that both cobalt(II) and nickel(II) have an octahedral configuration (cobalt(II) has 4.8–5.2 B.M. and nickel(II) 3.1–3.6 B.M.<sup>10</sup>), but it is not easy to deduce the configuration from the magnetic moment alone.

Detailed assignments for observed bands were made by comparing them with ligand, ligand sodium salt,

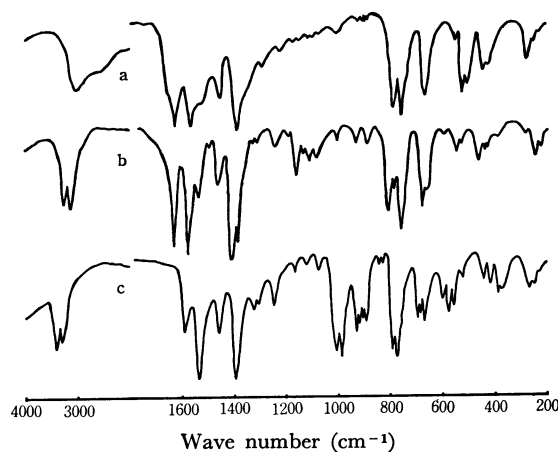


Fig. 3. Infrared absorption spectra of *p*-aminobenzoic acid and its coordination compounds in KBr discs. *a*=*p*-aminobenzoic acid, *b*=Cu(II), *c*=Ni(II)

TABLE 3. OBSERVED FREQUENCIES AND ASSIGNMENTS FOR METAL-*p*-AMINOBENZOIC ACID COORDINATION COMPOUNDS (cm<sup>-1</sup>)

Ni(II)	Cd(II)	Cu(II)	Pd(II)	Assignments
3183 s	3350 m	3226 m	3178 m	NH <sub>2</sub> asym. str.
3030 sh	3140 sh	3177 m	3071 m	NH <sub>2</sub> sym. str.
1604 s	1605 s	1611 s		C=C str.
1504 vs	1511 s	1580 vs	1602 vs	COO <sup>-</sup> asym. str.
		1571 s	1552 s	C=C str.
		1538 m	1507 s	
		1512 m		
1430 w	1423 sh	1437 s	1436 m	C=C str.
1372 vs	1389 vs	1385 vs	1349 vs	COO <sup>-</sup> sym. str.
1300 vw	1304 vw	1302 vw	1303 sh	
1239 m	1255 w	1247 w	1250 w	CN str.
1176 m	1175 m	1175 w	1171 s	
1143 w	1139 vw	1146 w		
1091 vw	1091 w			CH in plane def.
1016 m	1015 w	1019 vw	1015 w	
972 s	954 sh	1124 m	1110 m	NH <sub>2</sub> wagging
954 m	935 m			
	864 m			
845 s	845 m	851 m	858 m	CH out of plane def.
816 m	804 w	782 sh	802 vw	
784 m	783 m	777 s	776 s	C=C def.
774 m				
693 m	698 m	695 m	696 m	C=C def.
628 m	626 m	639 s	632 m	C=C def.
		552 vw	542 m	
		527 w		
514 m	507 w	489 m	503 w	C=C def.
432 m	409 m	445 m	454 w	COO <sup>-</sup> rocking
363 m		405 vw	441 w	MN str.
384 w		384 w	380 w	CN def.
			330 w	
288 w		298 m	296 w	CN def.
		281 sh		
264 m	266 m	259 vw	240 w	C-C def.
		211 w	223 v	MO str.

Abbreviations: s=strong, m=medium, w=weak, sh=shoulder

ligand hydrochloride,<sup>13)</sup> deuterated compound of metal coordination compounds, *m*-chlorobenzoic acid,<sup>14)</sup> *m*-chloroaniline,<sup>15)</sup> and *m*-dichlorobenzene.<sup>16)</sup> The results are shown in Table 2.

*p*-Aminobenzoic Acid Coordination Compounds. The infrared spectra of copper(II) and nickel(II) *p*-aminobenzoic acid coordination compounds and ligand are shown in Fig. 3 and their detailed assignments in Table 3. The assignments have been made by the same method as for the metal *m*-aminobenzoic acid coordination compounds. These spectra indicate that the compounds are also classified into two groups, one group including palladium(II) and copper(II) and the other cadmium(II) and nickel(II).

By the same discussions as for metal *m*-aminobenzoic

acid coordination compounds, such as the shifts of  $\text{NH}_2$  and  $\text{COO}^-$  stretching vibrations, existence of new peaks due to metal–nitrogen and metal–oxygen stretching vibrations, disappearance of absorption bands due to  $\text{COOH}$  and the elemental analysis of these compounds, it is clear that the coordination with metal has occurred through both nitrogen and oxygen in metal *p*-aminobenzoic acid coordination compounds as in metal *m*-aminobenzoic acid. This also differs from the results of Alyariya *et al.*<sup>7)</sup> in which the nitrogen was only coordinated to cadmium(II).

The magnetic moment of nickel(II) (3.37 B.M.) indicates that nickel(II) has an octahedral configuration<sup>10)</sup> but the configuration could not be determined from magnetic moment alone.

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