Studies of Bivalent Metal Complexes of 2-Acetylpyridine[1]

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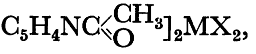
Bivalent metal complexes of 2-acetylpyridine (abbreviated as 2AP), $M(2AP)_2X_2$, M being copper, nickel, cobalt, and zinc ions and X being chloride, bromide, and iodide ions, were synthesized in ethanol solutions. The far-infrared analyses were discussed with reference to their structures, which were determined by means of the magnetic moments and the diffuse reflectance spectra. Except for $Co(2AP)_2Cl_2$ and $Co(2AP)_2I_2$, an octahedral structure was suggested for the $M(2AP)_2X_2$ complexes. A tetrahedral structure was assigned to $Co(2AP)_2Cl_2$ and $Co(2AP)_2I_2$ on the basis of their magnetic moments of 4.55 and 4.25 B.M. respectively and the diffuse reflectance spectra. The stretching vibrations of metal-nitrogen, metal-oxygen, and metal-halogen have been discussed.

Only a few spectrochemical studies have been reported on the metal complexes of 2-acetylpyridine, Karson,[2,3] however, studied the neutral metal complexes of  $[C_5H_4NC{<}^{CH_2}_{O^-}]_2M$ being formed in aqueous solutions, where the metals were bivalent ions of copper, nickel, and cobalt. He also reported the cationic-metal-complex formation of 2-acetylpyridine in ethanol solutions, *i.e.*,  $[C_5H_4NC{<}^{CH_3}_{O}]_2MX_2$, where the metals were the same as those of the neutral complexes and where X were chloride, bromide, and iodide ions, but he gave no detailed discussion.

For a better understanding of the biologically-important amide group, the present authors attempted studies of the cationic-metal complexes with 2-acetylpyridine (abbreviated as 2AP in this paper) in a series of 2-substituted pyridine-metal complexes. In analysing the data for 2AP-metal complexes, reference was made to the metal complexes of pyridine-2-carboxamide, since their structures and coordination sites have been determined by Yamasaki and Sekizaki,[4-8] the conclusion was confirmed by Masuko *et al.*[9]

This paper will deal with the magnetic moments and diffuse reflectance spectra for the determination of the structures of the complexes obtained, together with the band assignments in the far-infrared region for those containing different halide ions.

Experimental

Materials. The 2-acetylpyridine was purchased from the Tokyo Kogyo Co., Ltd., and was used without further purification. The bivalent metal halides (Cu, Ni, Co, and Zn) were special-grade products of Wako Pure Chemical Industries, Ltd.

Preparation of Complexes. 1) *Dihalogenobis(2-acetylpyridine)copper(II)*: To 10 ml of an ethanolic solution containing 0.48 g (4 mmol) of the ligand, we added 0.34 g (2 mmol) of copper(II) chloride dihydrate dissolved in 10 ml of ethanol. Immediately a dark green powder was precipitated, it was then washed with ethanol. The same procedure was used to obtain the bromo complex by the addition of the ligand, together with copper bromide in ethanol. A yellowish-green powder was precipitated.

Found: C, 44.06; H, 3.77; N, 7.28; Cu, 16.7%. Calcd for $Cu(C_7H_7ON)_2Cl_2 \cdot 1/4H_2O$: C, 44.12; H, 3.84; N, 7.35; Cu, 16.3%.

Found: C, 35.32; H, 3.12; N, 5.84; Cu, 12.7%. Calcd for $Cu(C_7H_7ON)_2Br_2 \cdot H_2O$: C, 35.10; H, 3.36; N, 5.84; Cu, 13.0%.

2) *Dihalogenobis(2-acetylpyridine)nickel(II)*: To 2 mmol of the ligand we added 4 mmol of nickel(II) chloride hexahydrate in 10 ml of ethanol, and the resultant solution was warmed gently on a water bath. A greenish-yellow powder was gradually precipitated. Bromo and iodo complexes were obtained as brown and reddish-brown precipitates by means of a procedure similar to that used for the chloro complex.

Found: C, 45.10; H, 3.85; N, 7.50; Ni, 15.8%. Calcd for $Ni(C_7H_7ON)_2Cl_2$: C, 45.21; H, 3.80; N, 7.53; Ni, 15.5%.

Found: C, 36.59; H, 3.18; N, 6.09; Ni, 12.7%. Calcd for $Ni(C_7H_7ON)_2Br_2$: C, 36.49; H, 3.06; N, 6.08; Ni, 12.8%.

Found: C, 30.35; H, 2.53; N, 4.86; Ni, 10.6%. Calcd for $Ni(C_7H_7ON)_2I_2$: C, 30.31; H, 2.53; N, 5.05; Ni, 10.6%.

3a) *Bis(2-acetylpyridine)cobalt(II) Halides*: To 2 mmol of the ligand in 10 ml of ethanol, we added 4 mmol of cobalt(II) chloride hexahydrate in 10 ml of ethanol, after which the solution was kept standing overnight at room temperature. A brown powder was thus precipitated. An iodide complex was obtained as a reddish-brown precipitate by means of the same procedure as was used for the chloride complex.

Found: C, 44.89; H, 3.69; N, 7.61; Co, 15.8%. Calcd for $Co(C_7H_7ON)_2Cl_2$: C, 45.19; H, 3.79; N, 7.35; Co, 15.5%.

Found: C, 30.35; H, 2.69; N, 5.11; Co, 10.4%. Calcd for $Co(C_7H_7ON)_2I_2$: C, 30.31; H, 2.55; N, 5.05; Co, 10.7%.

3b) *Dibromobis(2-acetylpyridine)cobalt(II)*: A bromo complex was obtained as a dark brown precipitate by means of the same procedure as was used for the chloride complex.

Found: C, 36.58; H, 3.22; N, 6.03; Co, 12.8%. Calcd for $Co(C_7H_7ON)_2Br_2$: C, 36.47; H, 3.06; N, 6.07; Co, 12.5%.

4) *Dihalogenobis(2-acetylpyridine)zinc(II)*: Two mmol of the ligand and 4 mmol of zinc chloride were dissolved in 10 ml of ethanol. After mixing the two solutions, the resultant solution was concentrated to half volume on a water bath and then kept standing overnight at room temperature. A yellowish-brown powder was thus precipitated. A bromo complex was obtained by mixing 2 mmol of zinc bromide and 4 mmol of the ligand in 30 ml of acetone. After the solution has been kept standing overnight at room temperature, a white crystalline precipitate was deposited out. An iodo complex was obtained as reddish-brown precipitate by means of the same procedure as was used for the chloro complex.

Found: C, 44.81; H, 3.74; N, 7.17; Zn, 16.9%. Calcd

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for $Zn(C_7H_7ON)_2Cl_2$: C, 44.42; H, 3.73; N, 7.40; Zn, 17.3%.

Found: C, 35.89; H, 2.97; N, 5.86; Zn, 14.0%. Calcd for $Zn(C_7H_7ON)_2Br_2$: C, 35.97; H, 3.02; N, 5.99; Zn, 14.3%.

Found: C, 29.58; H, 2.85; N, 4.99; Zn, 11.6%. Calcd for $Zn(C_7H_7ON)_2I_2$: C, 29.95; H, 2.51; N, 4.75; Zn, 11.4%.

Magnetic and Spectroscopic Measurements. The magnetic moments were determined by the Curie method with a Shimadzu MB-2-type magnetic balance at room temperature (18—21 °C). The diffuse reflectance spectra were measured with a Hitachi EPS-3T spectrophotometer equipped with an integrating sphere accessory. For the measurements, the complexes were diluted to 0.25 molality with magnesium oxide, and from 150 mg of the mixture pellets were prepared under a 600 kg/cm^2 pressure after evacuation. A Nihon Bunko IRA-2 spectrophotometer was used to record the infrared spectra in the region from 4000 to 400 cm^{-1}. The infrared spectra were measured with KBr discs, Nujol, and HCB mulls. For the measurements of the far-infrared spectra from 600 to 200 cm^{-1}, a Nihon Bunko DS-701G spectrophotometer was used. Solid samples were measured as mulls in Nujol; they were placed between two polyethylene films and inserted into a holder. The spectrum of the ligand was measured as a thin liquid layer placed between two polyethylene films.

Results and Discussion

Magnetic Moments. The magnetic moments observed for the 2AP-metal complexes are listed in Table 1. The magnetic moments of the copper complexes are a little lower than that of the spin-only formula, but the presence of copper–copper interaction usually produces a much larger decrease in the magnetic moment. Therefore, they may exist as mononuclear complexes. The magnetic-moment values of the nickel complexes are around 3.0 B.M., corresponding to the reported values of 2.9—3.4 B.M. for octahedral nickel complexes. As for the cobalt complexes, the bromo complex has a higher magnetic moment (5.40 B.M.) than those of the chloride and the iodide (4.55 and 4.25 B.M. respectively). These values indicate an octahedral structure for the bromo complex and a tetrahedral structure for the other two complexes.

TABLE 1. MAGNETIC MOMENTS OF 2-ACETYLPYRIDINE–METAL COMPLEXES

Complexes	Found	Calcd for the spin-only formula
$Cu(2AP)_2Cl_2\cdot 1/4H_2O$	1.69 B.M.	1.73 B.M.
$Cu(2AP)_2Br_2\cdot H_2O$	1.66	1.73
$Ni(2AP)_2Cl_2$	3.02	2.82
$Ni(2AP)_2Br_2$	3.00	2.82
$Ni(2AP)_2I_2$	2.97	2.82
$Co(2AP)_2CoCl_2$	4.55	3.88
$Co(2AP)_2CoBr_2$	5.40	3.88
$Co(2AP)_2CoI_2$	4.25	3.88
$Zn(2AP)_2Cl_2$	Diamagnetic	
$Zn(2AP)_2Br_2$	Diamagnetic	
$Zn(2AP)_2I_2$	Diamagnetic	

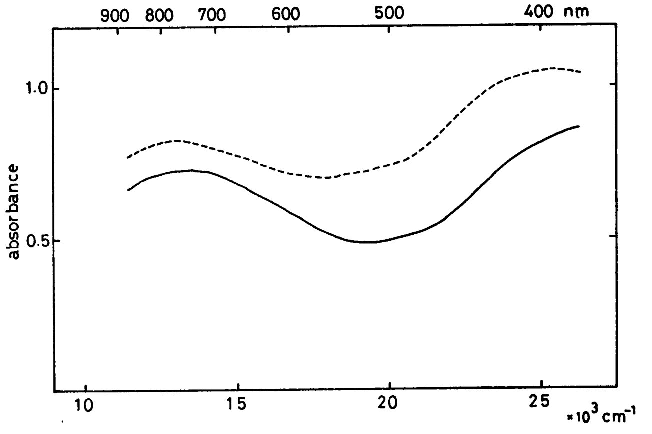

Fig. 1. Absorption spectra of $Cu(2AP)_2X_2$ measured by the diffuse reflectance method.
Solid line: X=Cl, Broken line: X=Br.

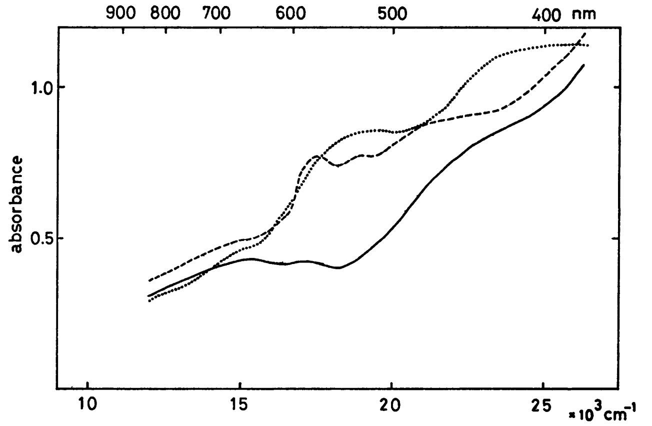

Fig. 2. Absorption spectra of $Ni(2AP)_2X_2$ measured by the diffuse reflectance method.
Solid line: X=Cl, Broken line: X=Br,
Dotted line: X=I.

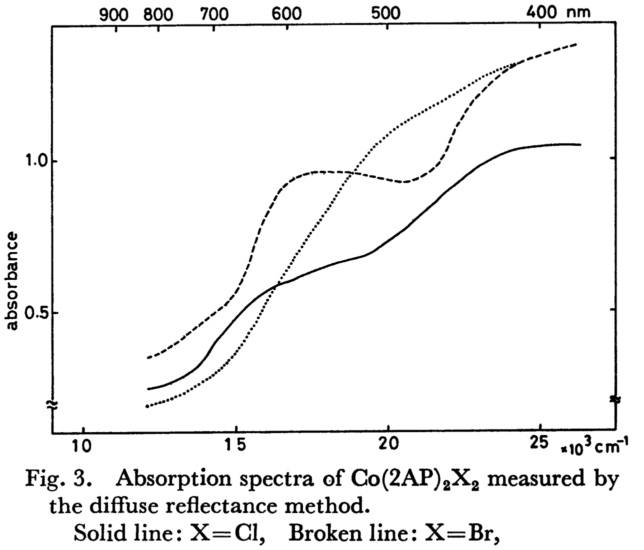

Fig. 3. Absorption spectra of $Co(2AP)_2X_2$ measured by the diffuse reflectance method.
Solid line: X=Cl, Broken line: X=Br,
Dotted line: X=I.

Diffuse Reflectance Spectra. The diffuse reflectance spectra of the complexes prepared are shown in Figs. 1—3. Both $Cu(2AP)_2Cl_2$ and $Cu(2AP)_2Br_2$ show d-d transition bands at 750 nm, the band at 390 nm for the bromo complex can be assigned to a charge-transfer band, whereas the corresponding band is not observed for the chloro complex, since the band is expected to appear there at a wavelength shorter than that of the bromo complex. The spectra of 2AP-copper complexes resemble that of the copper complex of pyridine-2-carboxamide,[5-7] the shift to the longer wavelength may be due to the difference in the coordinated aquo molecule and halide ions, so the same distorted octahedral structure is conceivable.

Figure 2 shows that $Ni(2AP)_2Cl_2$ gives d-d transition bands at 580 and 660 nm, while for $Ni(2AP)_2Br_2$ only one band, at 530 nm and with a shoulder at 760 nm, is observed. $Ni(2AP)_2I_2$ shows d-d transition bands at 510 and 670 nm, the latter being observed only as a shoulder. The additional band at 390 nm, characteristic of the iodo complex, may be due to the charge transfer. Moreover, the fact that the absorbance of the nickel complexes is nearly the same as those of the copper and cobalt complexes may indicate an octahedral structure for $Ni(2AP)_2X_2$, because one of the characteristic features of tetrahedral nickel complexes is that the molar absorption coefficient is relatively higher than those of the corresponding first-transition-metal complexes. Therefore, the d-d bands observed may be assignable to the $^3A_{2g}\rightarrow^3T_{1g}$ transition and the splitting may be due to the mixing of the spin orbital of $^3T_{1g}(F)$ and ^1E_g, as has been reported for the hexaaquonickel(II) complex.[10]

Figure 3 shows that, among the $Co(2AP)_2X_2$ complexes only $Co(2AP)_2Br_2$ indicates a d-d transition band at 560 nm, while for $Co(2AP)_2Cl_2$ and $Co(2AP)_2I_2$ only shoulders around 650 and 500 nm respectively are observed. The band of the bromo complex is characteristic of an octahedral cobalt complex and may be assigned to the $^4T_{1g}(F)\rightarrow^4T_{1g}(P)$ transition.[11] However, for the other two complexes no conclusion has yet been deduced for their structures, because they show no absorption maxima.

Infrared Spectra. In the region of 1700—1500 cm^{-1} some characteristic bands due to the carbonyl group and pyridine-ring vibrations are observed in the metal complexes. These bands are shown in Figs. 4 and 5, together with that of the ligand. The stretching vibration of the carbonyl group of the ligand appears at 1700 cm^{-1}, while those of C=N and C=C in the pyridine ring appear at 1582 and 1565 cm^{-1}. Upon complex formation the stretching vibration of the carbonyl group shifts to lower frequencies, while the peak at 1582 cm^{-1} shifts to frequencies a little higher. However, the peak at 1565 cm^{-1} does not shift at all. The lower-frequency shifts of the carbonyl group indicate an interaction between the metals and the oxygen atom, while the higher-frequency shifts of the peak at 1582 cm^{-1} may suggest a bond formation of the metals and the ring nitrogen, for the dipolar contribution of $C=N^+$ in the pyridine ring increases, as has been observed in pyridine hydrogen chloride.[12,13] These stretching vibrations of C=N are not metal-sensitive and appear at a constant frequency of 1595 cm^{-1}; however, the order of shifts to lower frequencies of the carbonyl-stretching vibrations is Ni>Co>Cu>Zn in the bromo complexes. The copper complexes give peaks at 1685 and 1683 cm^{-1} for the chloro and the bromo complexes; those frequencies are higher than those of the other metal complexes examined, indicating a weaker interaction of copper with the oxygen atom. For the nickel complexes, the lower-frequency shifts of the carbonyl group depend on the halide ions; the shifts are observed in the following order of Cl>Br>I: 1665, 1653, and 1650 cm^{-1}.

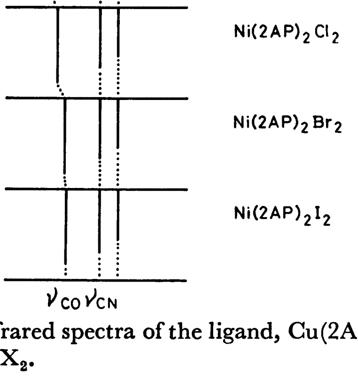

Fig. 4. Infrared spectra of the ligand, $Cu(2AP)_2X_2$, and $Ni(2AP)_2X_2$.

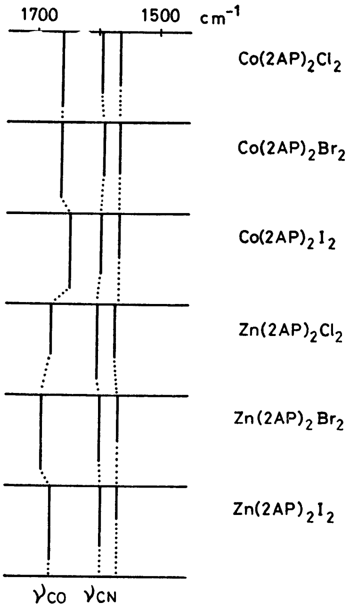

Fig. 5. Infrared spectra of $Co(2AP)_2X_2$ and $Zn(2AP)_2X_2$.

The chloro complex of zinc, whose peak due to the carbonyl group appears at 1675 cm^{-1}, giving a somewhat different spectrum from those of the other two metal complexes, perhaps suggesting its structural difference. A remarkable difference in the far-infrared spectrum is alo observed; the question will be discussed more detail below. The bromo and iodo complexes give peaks at 1688 and 1675 cm^{-1}; it may be considered from these shifts that zinc forms a weaker bond than those of the cobalt and nickel complexes.

These frequency shifts of the carbonyl group and the pyridine ring may lead to the conclusion of the chelate ring formation, which can easily be understood in view of the ligand structure and confirmed by the far-infrared data.

Table 2. Far-infraredral data for bivalent metal complexes of pyridine and α-picoline (in cm^{-1})

Complexes	ν_{M-N}	ν_{M-X}	Structure
$CuCl_2 \cdot 2py$[a]	268	235(b)[b] 294(t)	Distorted polymeric octahedral
$CuBr_2 \cdot 2py$	269	202(b) 255(t)	
trans-$NiCl_2 \cdot 4py$	236	246	Monomeric octahedral
trans-$NiBr_2 \cdot 4py$	235	200	
trans-$NiI_2 \cdot 4py$	240, 228	200	
$NiCl_2 \cdot 2(\alpha\text{-pic})$[a]	239, 227	327, 297	Tetrahedral
$NiBr_2 \cdot 2(\alpha\text{-pic})$	239	256	
trans-$CoCl_2 \cdot 4py$	217	230	Monomeric octahedral
trans-$CoBr_2 \cdot 4py$	200	214	
$CoCl_2 \cdot 2py$	252	340, 304	Tetrahedral
$CoBr_2 \cdot 2py$	250	274, 242	
$CoI_2 \cdot 2py$	237	246	
$ZnCl_2 \cdot 2py$	220	329, 296	Tetrahedral
$ZnBr_2 \cdot 2py$	220	254	

a) In this table py and α-pic denote pyridine and α-picoline, respectively. b) Small letters in parentheses, *i.e.*, t and b, denotes terminal and bridging halides, respectively.

Far-infrared Spectra. There have been accumulated very many data, especially concerning metal-halide complexes of pyridine and its derivatives, indicating that a change in halide ions does not affect the stretching vibrations of the metal-ligand; therefore, the absorption peaks which do remain at a fairly constant frequency upon the variation in the halide ions are attributable to the metal-ligand vibrations in $M(2AP)_2X_2$. Some far-infrared data of pyridine-metal complexes are shown in Table 2; they were utilized for the analyses of the spectra of $M(2AP)_2X_2$. The structural change has been proved to have remarkable effects on the stretching vibrations of the metal-halide and the metal-ligand. Moreover, for the $M(2AP)_2X_2$ complexes the far-infrared data present valuable information for the determination of their structures. In assigning the stretching vibrations of metal-ligand and metal-halide in $M(2AP)_2X_2$, the chelate ring formation is taken into account to produce the objective stretching vibrations at higher frequencies than those of the corresponding metal-pyridine complexes.

The far-infrared spectra of $M(2AP)_2X_2$ in the region of 600—200 cm^{-1} are shown in Figs. 6—9.

As is shown in Fig. 6, 2AP gives peaks at 593 and 412 cm^{-1} assignable to the in-plane and out-of-plane ring bending. The peak at 485 cm^{-1} may be assignable to the in-plane deformation mode of the acetyl group, while the peaks at 360 and 213 cm^{-1} are attributable to the pyridine-ring vibration and the acetyl torsion respectively.

$Cu(2AP)_2X_2$. Figure 6 shows the far-infrared spectra of $Cu(2AP)_2X_2$. The chloro complex has a strong but broad band at 275 cm^{-1}, with shoulders at 290 and 250 cm^{-1}. The bromo complex shows three bands, at 290, 250, and 225 cm^{-1}. Therefore, the common bands at 290 and 250 cm^{-1} are assignable to the chelate-ring vibrations, the former being mainly due to the stretching vibration of copper-nitrogen, and the latter, to that of copper-oxygen. The stretching vibration of copper-chloride may be assignable to the band at 275 cm^{-1}, and that of copper-bromide, to the band at 225 cm^{-1}, which is shifted 20—30 cm^{-1} toward the lower-frequency side than those of the terminal halide-copper in $CuX_2 \cdot 2py$ (py=pyridine). The theoretical prediction for infrared-active bands in octa-

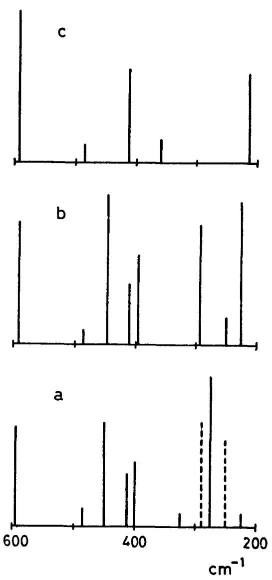

Fig. 6. Far-infrared spectra of the ligand and $Cu(2AP)_2X_2$.
a: X=Cl, b: X=Br, c: Ligand
broken line: Shoulder

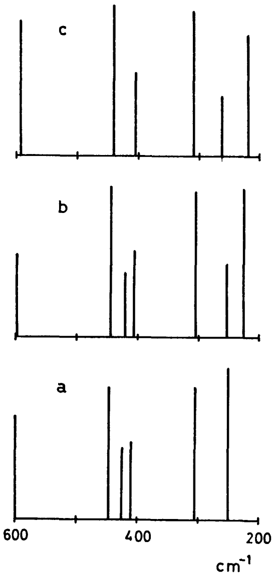

Fig. 7. Far-infrared spectra of $Ni(2AP)_2X_2$.
a: X=Cl, b: X=Br, c: X=I.

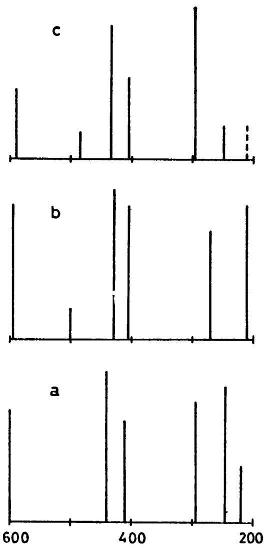

Fig. 8. Far-infrared spectra of $Co(2AP)_2X_2$.
a: X=Cl, b: X=Br, c: X=I,
broken line: shoulder

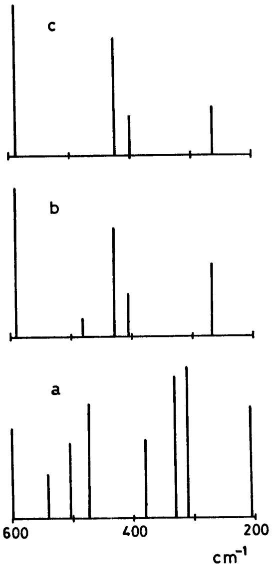

Fig. 9. Far-infrared spectra of $Zn(2AP)_2X_2$.
a: X=Cl, b: X=Br, c: X=I

hedral $Cu(2AP)_2X_2$ coincides with the number of bands observed; therefore, an octahedral structure with a *trans*-planar coordination of 2AP with halide ions bonded to the copper ion perpendicular to the chelate ring may be proposed.

Ni(2AP)$_2$X$_2$. Because of the chelate-ring formation in nickel complexes of 2AP, the bond distances between the nickel ion and the nitrogen atom will be shortened and the stretching vibrations may be expected to appear at higher frequencies than those of NiX_2–4py (py=pyridine). As is shown in Fig. 7, among the halogeno complexes examined only the chloro complex gives a band at 250 cm^{-1} assignable to the stretching vibration of nickel-chloride. The common bands are observed around 310—305 cm^{-1} and 260—250 cm^{-1}. These spectra of $Ni(2AP)_2X_2$, resembling those of octahedral $NiX_2 \cdot 4py$ (py=pyridine) rather than those of tetrahedral $NiCl_2(\alpha\text{-picoline})_2$, suggest a *trans*-planar octahedral structure.

Co(2AP)$_2$X$_2$. Since $Co(2AP)_2Cl_2$ and $Co(2AP)_2I_2$ are considered to have a tetrahedral structure belonging to the C_{2v} point group, four infrared-active cobalt-2AP stretching bands are expected to appear. However, only three bands are observed for these complexes, as is shown in Fig. 8, the missing band, due to the symmetric cobalt-oxygen stretching vibration, may appear below 200 cm^{-1}. The magnetic moment indicates an octahedral structure for $Co(2AP)_2Br_2$, where if 2AP coordinates in a *trans*-planar configuration two cobalt-2AP stretching vibrations should appear. This is the case in the bromo complex, for only two bands attributable to the stretching vibrations of cobalt-nitrogen and cobalt-oxygen are observed.

Zn(2AP)$_2$X$_2$. Among the $Zn(2AP)_2X_2$ complexes the bands about 265 cm^{-1} are consistent except for the chloro complex and may be assigned to the stretching bands of zinc-nitrogen. The chloro complex gives two bands, at 330 and 310 cm^{-1}, which are close to the asymmetric and symmetric stretching bands of zinc-chloride in tetrahedral $ZnCl_2 \cdot 2py$ (py=pyridine).[14] Therefore, they can be assigned to the asymmetric and symmetric stretching bands of zinc-chloride, indicating a *cis*-conformation of the chloride ions in $Zn(2AP)_2Cl_2$. It is sure that the chloro complex has structure different from that of the other two complexes, but the unavailability of magnetic moments and diffuse reflectance spectra makes it difficult to draw any definite conclusions.

TABLE 3. EXPERIMENTAL ASSIGNMENTS OF 2-ACETYLPYRIDINE–METAL COMPLEXES IN THE FAR-INFRARED REGION

Complexes	ν_{M-X}	ν_{M-N}	ν_{M-O}	Unassigned
$Cu(2AP)_2Cl_2$	275	(290)[a]	(250)	
$Cu(2AP)_2Br_2$	225	293	250	
$Ni(2AP)_2Cl_2$	250	305	(250)	
$Ni(2AP)_2Br_2$		305	253	226
$Ni(2AP)_2I_2$		310	263	218
$Co(2AP)_2Cl_2$		296 245	218	
$Co(2AP)_2Br_2$		270	210	
$Co(2AP)_2I_2$		293 247	(215)	
$Zn(2AP)_2Cl_2$	330 310	205		
$Zn(2AP)_2Br_2$		267		
$Zn(2AP)_2I_2$		263		

a) Parenthesis denotes a shoulder.

Our experimental assignments of the far-infrared spectra are listed in Table 3. When the $M(2AP)_2X_2$ complexes are compared with $[M(piaH)_2(H_2O)_2]Cl_2$ (piaH=pyridine-2-carboxamide) from the standpoint of the far-infrared spectra, the former complexes have the following characteristics:

1) The existence of the chelate-ring vibrations of $M(2AP)_2X_2$ at frequencies lower than those of the corresponding $[M(piaH)_2(H_2O)_2]Cl_2$ may suggest lower

stability constants in the former than in the latter.

2) $Cu(2AP)_2X_2$ gives the copper-2AP stretching vibrations at frequencies rather lower than the other $M(2AP)_2X_2$ complexes.

3) $Co(2AP)_2Cl_2$ and $Co(2AP)_2I_2$ have a tendency to take a tetrahedral structure.

4) In $Zn(2AP)_2Cl_2$ the coordination of the chloride ion to zinc is in the *cis*-configuration.

Conclusion

Through the analyses of the magnetic moments, the diffuse reflectance spectra, and the infrared spectra, the following structures can be tentatively proposed for $M(2AP)_2X_2$. $Cu(2AP)_2X_2$ ($X=Cl^-$ and Br^-) are considered to have a mononuclear distorted octahedral structure, with a *trans*-planar conformation of the 2AP molecules to copper. For $Ni(2AP)_2X_2$ ($X=Cl^-$, Br^-, and I^-), an octahedral structure with a *trans*-planar coordination of 2AP is proposed. A tetrahedral structure may be assigned to $Co(2AP)_2Cl_2$ and $Co(2AP)_2I_2$, while for $Co(2AP)_2Br_2$ an octahedral structure with a *trans*-planar coordination of 2AP is supported.

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