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Studies of Bivalent Metal Chelates of 2-Aminomethylpyridine

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Bivalent metal chelates of 2-aminomethylpyridine (abbreviated as 2AMP), $M(2AMP)_2X_2$ (M=Cu, Ni, Co, and Zn ion; X=Cl^-, Br^-, I^-), were synthesized in ethanol. The magnetic moments and the diffuse reflectance spectra were measured. The $Cu(2AMP)_2X_2$ complexes (X=Cl^- and Br^-) were considered to have a monomeric distorted octahedral structure. The $Ni(2AMP)_2X_2$ complexes (X=Cl^-, Br^-, I^-) were also suggested to have an octahedral structure. However, for $Co(2AMP)_2Br_2$ and $Co(2AMP)_2I_2$ a tetrahedral and a square planar structure were proposed on the basis of their magnetic moments of 4.20 and 2.78 B.M. respectively. The infrared spectra of the chelates were analysed in relation to their structures; a good relationship was found between the structures and the far-infrared spectra.

Various metal chelates of 2-aminomethylpyridine have been studied by Sutton[1–3] and Michelsen[4] with regard to their electronic absorption spectra and magnetic moments. The stability constants were reported by Walter *et al.*[5] and Goldberg.[6] However, no infrared spectroscopic investigation of these chelates has ever been made. The present authors have now synthesized bivalent metal chelates of 2-aminomethylpyridine (abbreviated as 2AMP in this paper) in ethanol, that is, $M(2AMP)_2X_2$ complexes, M being copper(II), nickel(II), cobalt(II), and zinc(II) ions and X being chloride, bromide, and iodide ions. Among these complexes, two cobalt chelates, $Co(2AMP)_2Br_2$ and $Co(2AMP)_2I_2$ were newly prepared, but the chloro chelate was not obtained in spite of several trials.

In order to study their structures, the magnetic moments and the diffuse reflectance spectra were measured. By referring these data, the far-infrared spectra were then analysed in relation to the structures of the chelates obtained.

Experimental

Materials. The 2-aminomethylpyridine, a product of the Aldrich Chemical Co., Ltd., was used without further purification. The metal halides used were analytical-grade products of Wako Pure Chemical Industries, Ltd.

Preparation of Chelates. *Bis(2-aminomethylpyridine)cobalt(II) Halides*: To a solution containing 0.43 g (4 mmol) of the ligand in 10 ml of ethanol, we added 0.44 g (2 mmol) of cobalt bromide dissolved in 20 ml of ethanol; a dark brown powder was thus precipitated. The precipitate was collected by filtration and washed with ethanol.

The corresponding iodide was synthesized by a procedure similar to that used for the bromide chelate, which was obtained as a reddish-brown powder.

Found: C, 31.77; H, 3.95; N, 12.43; Co, 13.2%. Calcd for $Co(C_6H_8N_2)_2Br_2 \cdot H_2O$: C, 31.81; H, 4.01; N, 12.36; Co, 13.0%.

Found: C, 27.55; H, 3.05; N, 10.71; Co, 11.2%. Calcd for $Co(C_6H_8N_2)_2I_2$: C, 27.24; H, 3.05; N, 10.59; Co, 11.1%.

The other metal chelates were synthesized in ethanol by treating 2 mmol of the metal halides with 4 mmol of the ligand. The results of the elemental analyses of the metal chelates obtained are shown in Table 1.

Magnetic and Spectroscopic Measurements. The magnetic moments were measured by the Curie method with a Shimadzu MB-2 magnetic balance at room temperature. The diffuse reflectance spectra were measured with a Hitachi EPS-3T spectrophotometer equipped with an integrating-sphere accessory. For the measurements the chelates were diluted to a 0.25 molality with magnesium oxide, and pellets containing 150 mg of the mixtures were prepared under a 600 kg/cm² 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 using the KBr disc method and the Nujol and HCB mull method. The far-infrared spectra in the region of 600—200 cm⁻¹ were measured with a Nihon Bunko DS-701G spectrophotometer using the Nujol mull method.

Table 1. Elemental analysis of $M(2AMP)_2X_2$

Chelates	Found (%)				Calcd (%)			
	C	H	N	M	C	H	N	M
$Cu(C_6H_8N_2)_2Cl_2$	40.95	4.68	15.90	17.7	41.09	4.60	15.97	18.1
$Cu(C_6H_8N_2)_2Br_2 \cdot 1/2H_2O$	32.09	3.57	12.57	14.4	32.13	3.82	12.49	14.2
$Ni(C_6H_8N_2)_2Cl_2 \cdot 3/4H_2O$	40.35	4.82	15.63	16.6	40.13	4.90	15.60	16.3
$Ni(C_6H_8N_2)_2Br_2$	32.87	3.56	12.83	13.6	33.15	3.71	12.88	13.5
$Ni(C_6H_8N_2)_2I_2$	27.10	3.02	10.59	11.2	27.25	3.05	10.59	11.1
$Zn(C_6H_8N_2)_2Cl_2 \cdot 1/4H_2O$	40.22	4.45	15.52	18.1	40.39	4.66	15.70	18.3
$Zn(C_6H_8N_2)_2Br_2$	32.72	3.45	12.73	14.5	32.65	3.65	12.69	14.9
$Zn(C_6H_8N_2)_2I_2$	26.87	3.00	10.45	12.4	26.91	3.01	10.46	12.2

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Results and Discussion

Magnetic Moments. The magnetic moments observed for $M(2AMP)_2X_2$ are listed in Table 2. The copper chelates give magnetic moments a little lower than that of the spin-only formula, indicating a negligible spin interaction among adjacent copper ions.

Table 2. Magnetic moments of $M(2AMP)_2X_2$ (19—21 °C)

Chelates	Observed	Calcd for spin-only formula
$Cu(2AMP)_2Cl_2$	1.64 B.M.	1.73 B.M.
$Cu(2AMP)_2Br_2$	1.71	1.73
$Ni(2AMP)_2Cl_2$	2.94	2.82
$Ni(2AMP)_2Br_2$	2.96	2.82
$Ni(2AMP)_2I_2$	2.94	2.82
$Co(2AMP)_2Br_2$	4.20	3.88
$Co(2AMP)_2I_2$	2.79	1.73
$Zn(2AMP)_2Cl_2$	Diamagnetic	
$Zn(2AMP)_2Br_2$	Diamagnetic	
$Zn(2AMP)_2I_2$	Diamagnetic	

The nickel chelates give values of the magnetic moments of 2.94—2.96 B.M., which are comparable to those reported for octahedral nickel complexes, *i.e.*, 2.9—3.4 B.M.

The magnetic moment of $Co(2AMP)_2Br_2$ is found to be 4.20 B.M., which is nearer to the values of 4.4—4.8 B.M. reported for tetrahedral cobalt complexes than to those of 4.7—5.2 B.M. for octahedral complexes.[7] On the other hand, $Co(2AMP)_2I_2$ gives a very low magnetic moment of 2.79 B.M., which can be related to the values of 2.4—2.8 B.M. reported for square planar cobalt complexes.[7]

All the zinc chelates show a diamagnetic character, as had been expected.

Diffuse Reflectance Spectra. The d-d transition bands appear at 610 nm, with a shoulder at 750 nm, for $Cu(2AMP)_2Cl_2$ and at 630 and 730 nm for $Cu(2AMP)_2Br_2$, as is shown in Fig. 1. The bands in the shorter-wavelength region are observed at a position similar to that of $Cu(2AMP)_2I_2$ in an aqueous solution, for which an octahedral structure has been proposed by Sutton.[8] Therefore, the same octahedral arrangement may be proposed for $Cu(2AMP)_2Cl_2$ and $Cu(2AMP)_2Br_2$, and the bands in the longer-wavelength region may arise from the orbital splitting due to a distortion from the octahedral configuration.

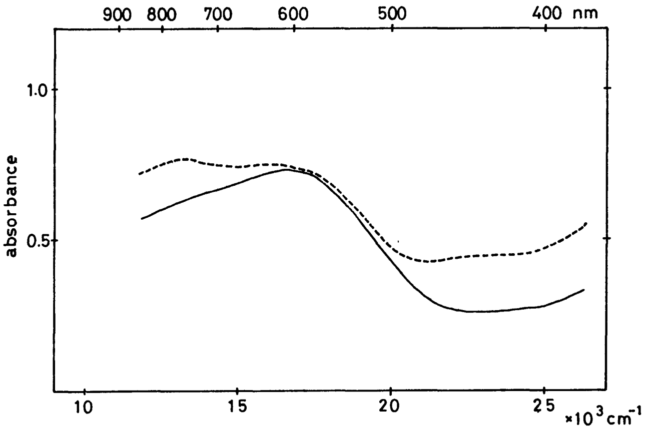

Fig. 1. Absorption spectra of $Cu(2AMP)_2X_2$ measured by the diffuse reflectance method.
—— $X=Cl^-$, ---- $X=Br^-$

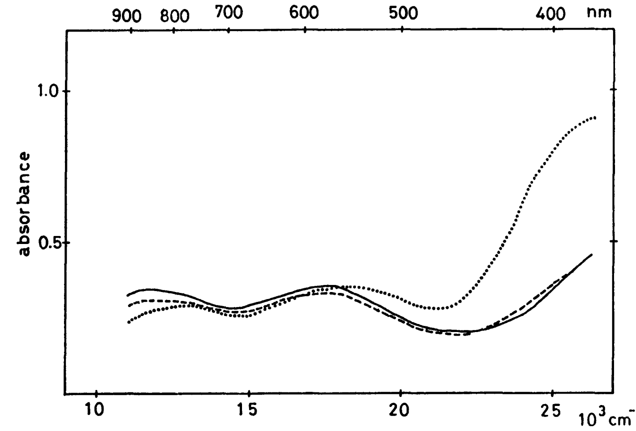

Fig. 2. Absorption spectra of $Ni(2AMP)_2X_2$ measured by the diffuse reflectance method.
—— $X=Cl^-$, ---- $X=Br^-$, ... $X=I^-$

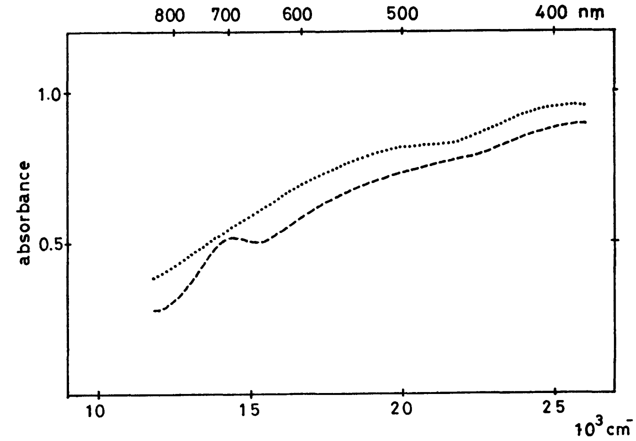

Fig. 3. Absorption spectra of $Co(2AMP)_2X_2$ measured by the diffuse reflectance method.
---- $X=Br$, ... $X=I$

As is shown in Fig. 2, the three nickel chelates, $Ni(2AMP)_2X_2$, show spectra similar to one another, all with the d-d bands around 560—570 nm. The strong band at 380 nm of the iodo chelate may be assignable to the CT band, and a band is also observed at 770 nm. The corresponding bands for the chloro and bromo chelates appear around 850 nm. These d-d bands, all with low intensities, are characteristic of octahedral nickel complexes, which usually have molar absorption coefficients of 1—10. These diffuse reflectance spectra resemble the electronic absorption spectra of $[Nien_2(H_2O)_2]$ and $[Nibip_2(H_2O)_2]$; therefore, an octahedral structure can be assigned to $Ni(2AMP)_2X_2$, as has been postulated by Sutton.[1] The d-d bands in the shorter-wavelength region can be assigned to the $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ and those in the longer-wavelength region, to the $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ transition.[9]

The absorption spectra of Co(2AMP)$_2$X$_2$ are shown in Fig. 3. Co(2AMP)$_2$Br$_2$ shows the d-d band at 710 nm, as is characteristic of tetrahedral cobalt complexes, and in the shoter-wavelength region no distinct absorption maximum is observed. Co(2AMP)$_2$I$_2$ gives a very broad band around 500 nm, which is overlapped by the CT band at 380 nm. However, there has been reported little information as to the electronic absorption spectra of planar cobalt complexes; therefore, no difinite conclusion can be drawn from the diffuse reflectance spectrum for the structure of the iodide chelate.

Infrared Spectra. The chelate ring formation between 2AMP and the metal ions would bring about a lower-frequency shift of the stretching vibration of the amino group. The ligand shows both the asymmetric and symmetric stretching vibrations due to the amino group at 3370 and 3300 cm^{-1} respectively. These bands shift to a frequency side lower by 100—200 cm^{-1} upon the chelate formation, as is shown in Fig. 4.

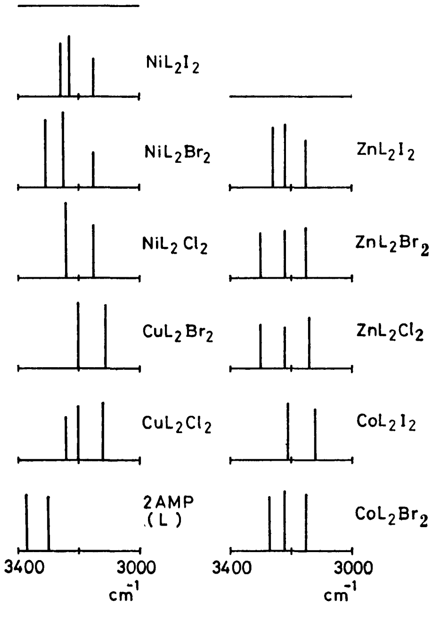

Fig. 4. Infrared spectra of 2AMP and M(2AMP)$_2$X$_2$ in the region of 3400—3000 cm^{-1}

The degree of the frequency shift is the largest for the copper chelates; among the other metal chelates, as is exemplified in the bromo system, the order of Cu(3200 cm^{-1})<Zn(3266 cm^{-1})<Co(3272 cm^{-1})<Ni(3305 cm^{-1}) is found for the asymmetric stretching vibrations. No regularity can be found in the effects of the halide ions on the stretching frequencies of the amino group.

The deformation frequency of the amino group in the ligand is observed at 1591 cm^{-1}; it shifts by about 10 cm^{-1} toward higher frequencies upon the chelate formation, contrary to the observation of the lower-frequency-side shifts of ammine complexes reported by Sacconi *et al.*[10]

Far Infrared Spectra. Figure 5 shows the far-infrared spectra of the ligand. It is very convenient to know that no peaks are observed below 400 cm^{-1}, since the metal complexes of pyridine derivatives usually bring about absorption peaks due to the metal-pyridine nitrogen stretching vibrations below 400 cm^{-1}.

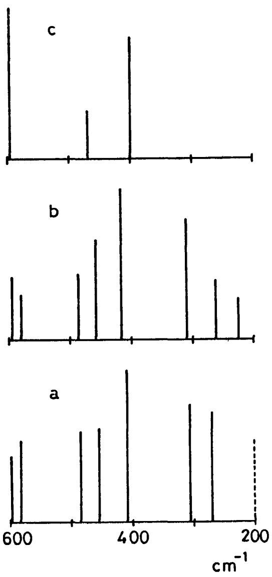

Fig. 5. Far-infrared spectra of 2AMP and Cu(2AMP)$_2$X$_2$
a: X=Cl, b: X=Br, broken line: shoulder
c: 2AMP

Cu(2AMP)$_2$X$_2$. The stretching vibration of copper-chloride is observed around 200 cm^{-1} as a broad peak; however, that of the copper-bromide is not observed above 200 cm^{-1}, as is shown in Fig. 5. The vibrations due to the chelate ring are found at 310—306 cm^{-1} and 270—263 cm^{-1}. The former may be assigned to the copper-amino nitrogen stretching, and the latter, to the copper-pyridine nitrogen stretching.

Clark and Williams[13] reported that the stretching vibration of copper-chloride in distorted octahedral pyridine complexes, CuCl$_2$·2py (py=pyridine), appeared at 294 and 235 cm^{-1} for the bridging-chloride and the terminal-chloride respectively. In this pyridine complex, the distance between the bridging-chloride and the copper ion was determined to be 3.05 Å by Dunitz,[14] but the peak at 200 cm^{-1} in Cu(2AMP)$_2$Cl$_2$ seems to indicate a longer bond distance between the chloride and the copper ion, with a stronger distortion from the octahedral structure than that of the pyridine complex. Therefore, a distorted octahedral structure is supported by the infrared spectra, coincinding with the result deduced from the magnetic moments and the diffuse reflectance spectra.

Ni(2AMP)$_2$X$_2$. As is shown in Fig. 6, the common peaks observed among the three nickel chelates are in two regions, 296—290 cm^{-1} and 255—250 cm^{-1}, which can be assigned to the nickel-amino nitrogen and the nickel-pyridine nitrogen stretching vibrations respectively. The nickel-chloride stretching is found at 205 cm^{-1}, and the corresponding peaks of the bromo and iodo chelates are not observed above 200 cm^{-1}. The additional peaks at 234 and 235 cm^{-1} of the bromo and iodo chelates are left unassigned. Since the octahedral nickel chelates with a *trans*-planar coordination of 2AMP molecules belong to the C$_{2h}$ point group, two peaks due to the Ni-2AMP stretching and one

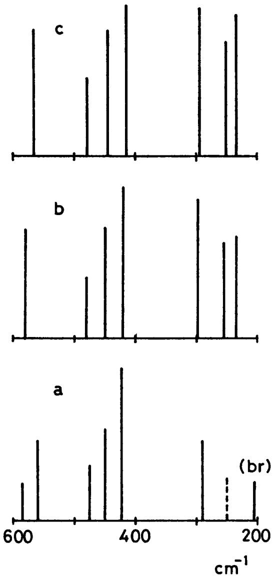

Fig. 6. Far-infrared spectra of $Ni(2AMP)_2X_2$
a: X=Cl, b: X=Br, c: X=I,
broken line: shoulder

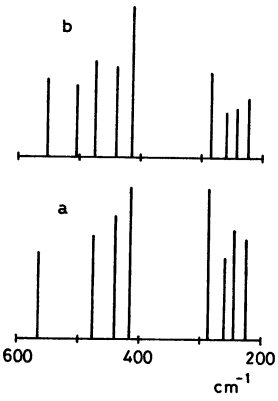

Fig. 7. Far-infrared spectra of $Co(2AMP)_2X_2$
a: X=Br, b: X=I

peak due to the nickel-halide stretching can be expected. Therefore, the far infrared spectra of $Ni(2AMP)_2X_2$ support an octahedral structure.

Co(2AMP)$_2$X$_2$. Figure 7 shows the far-infrared spectra of $Co(2AMP)_2X_2$. As it has been proposed from the magnetic moment that the bromide chelate is in a tetrahedral configuration which belongs to the C_{2v} point group, four Co-2AMP stretching bands can be expected. The measured spectrum of $Co(2AMP)_2Br_2$ shows four peaks assignable to Co-2AMP stretching vibrations and supports the tetrahedral structure.

The iodide chelate, which may be supposed from the magnetic moment to have a square planar configuration, also shows four peaks attributable to Co-2AMP stretching vibrations. If 2AMP molecules coordinate to cobalt ions in a *trans*-planar form belonging to the C_{2h} point group, two Co-2AMP stretching vibrations should appear. On the other hand, a *cis*-planar configuration, belonging to the C_{2v} point group, should bring about four Co-2AMP stretching vibrations; this is what is found for the iodide chelate.

Zn(2AMP)$_2$X$_2$. For the three zinc chelates, consistent peaks are observed in the regions of 243—240 cm^{-1} and 210—205 cm^{-1}. The peak at 270 cm^{-1} is characteristic of the chloro chelate and is assigned to the zinc-chloride stretching. These data seem to indicate an octahedral structure for the zinc chelates, with a *trans*-planar coordination of the 2AMP molecules to the zinc ion. The far-infrared assignments are listed in Table 3.

Table 3. The assignments of metal–nitrogen stretching frequencies of $M(2AMP)_2X_2$ (cm^{-1})

Chelates	ν_{M-X}	$\nu_{M-N\,(amino)}$	$\nu_{M-N\,(pyridine)}$	Unassigned
$Cu(2AMP)_2Cl_2$	200	306	270	
$Cu(2AMP)_2Br_2$		310	263	225
$Ni(2AMP)_2Cl_2$	205	290	250	
$Ni(2AMP)_2Br_2$		296	255	235
$Ni(2AMP)_2I_2$		296	252	234
$Co(2AMP)_2Br_2$		287(asym.)	245(asym.)	
		260(sym.)	224(sym.)	
$Co(2AMP)_2I_2$		287(asym.)	243(asym.)	
		260(sym.)	223(sym.)	
$Zn(2AMP)_2Cl_2$	270	240	210	
$Zn(2AMP)_2Br_2$		243	210	
$Zn(2AMP)_2I_2$		240	205	

The assignment of the metal-amino nitrogen to the higher-frequency region of the metal-2AMP stretching vibrations is made on the basis of the basicities of the objective nitrogen atoms. The dissociation constants of 2AMP have been reported to be $10^{-2.14}$ and $10^{-8.57}$ for the pyridine ring nitrogen and the amino nitrogen[11] respectively. The correlation between the p*K* values of the ligands and stability constants in heterocyclic ammine complexes with the silver ion has been reported to show a trend for the ligand with a higher p*K* value to have a larger stability constant.[12] This relationship can also be applied to other metal complexes. In the chelate ring of 2AMP with the bivalent metal ions, the linkage between the amino nitrogen and the metal ions may be much stronger than that of the pyridine nitrogen with the same metal ions, so that the former stretching vibration can be expected to appear at a higher frequency than that of the latter.

In order to ascertain the validity of the assignments

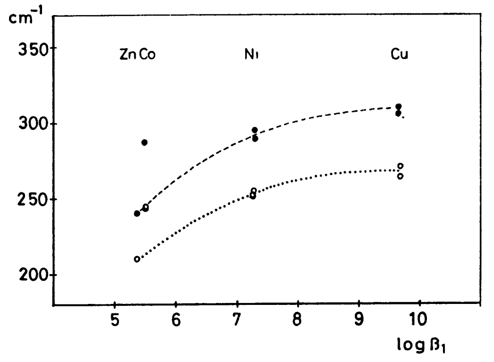

Fig. 8. Plots of M-N(amino) and M-N(pyridine) stretching frequencies *vs*. log β_1 for $M(2AMP)_2X_2$.
—●—●—●— M-N(amino)
···○···○···○··· M-N(pyridine)

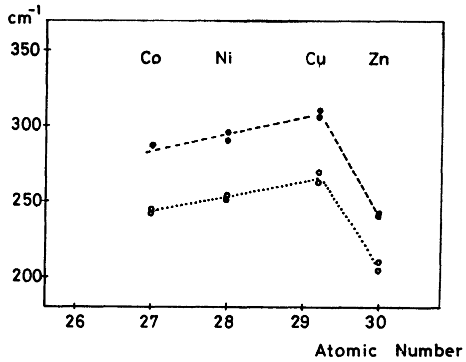

Fig. 9. Plots of M-N(amino) and M-N(pyridine) stretching frequencies *vs.* atomic number for $M(2AMP)_2X_2$.
—●—●—●— M-N(amino)
···○···○···○··· M-N(pyridine)

in the far-infrared spectra, plots were made of the metal-nitrogen stretching vibrations against the stability constants ($\log \beta_1$) of $M(2AMP)_2X_2$ in aqueous solutions, as is shown in Fig. 8. The deviation of the cobalt chelates from the tendency shown by the other metal chelates may be attributed to their structural differences. However, the general trend for the metal-amino nitrogen stretching frequencies of the bromo chelates is in the following order; Zn(243 cm^{-1})<Cu(310 cm^{-1})> Ni(296 cm^{-1})>Co(287 cm^{-1}), coinciding with the Irving-Williams stability order. A further correlation, as is shown in Fig. 9, exists between the metal-2AMP stretching frequencies and the atomic numbers of the metal ions. The order found is the same as in the case of the stability constants; the Irving-Williams order also holds in spite of their structural differences.

Conclusion

The structures of the $M(2AMP)_2X_2$ complexes were studied by means of the magnetic moments, the diffuse reflectance spectra, and the far-infrared spectra. The $Cu(2AMP)_2X_2$ complexes are considered to have a monomeric distorted octahedral structure, while for $Ni(2AMP)_2X_2$ an octahedral configuration is proposed. The $Co(2AMP)_2Br_2$ complex has the magnetic moment of 4.20 B.M., and electronic absorption maximum at 710 nm, and four Co-2AMP stretching bands; therefore, an tetrahedral structure is proposed. A *trans*-planar configuration may be suitable for $Co(2AMP)_2I_2$, which has a very low magnetic moment of 2.79 B.M. and four Co-2AMP stretching vibrations in the far-infrared region. Only far-infrared spectra are available for $Zn(2AMP)_2X_2$, but the similarity of the spectra and the existence of the zinc-chloride stretching vibration seems to indicate an octahedral structure for the zinc chelates. The order of Zn<Cu>Ni>Co is found in the tentatively-assigned metal-2AMP stretching vibrations, coinciding with the Irving-Williams stability order.

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