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The Copper(II), Nickel(II) and Palladium(II) Complexes of Pyridine-2-acetamide

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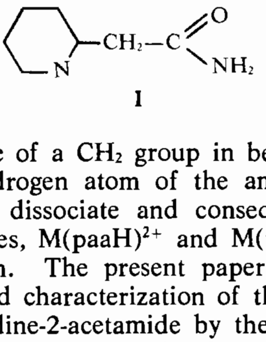
The 1:1 and 1:2 copper(II), nickel(II) and palladium(II) complexes of pyridine-2-acetamide (abbreviation, paaH), α– and β–$CuCl_2(paaH)$, $CuBr_2(paaH)$, $CuCl_2(paaH)_2$, $CuBr_2(paaH)_2$, $Cu(ClO_4)_2(paaH)_2$, $NiCl_2(paaH)_2 . 2H_2O$, $PdCl_2(paaH)_2$ and $PdBr_2(paaH)_2$, were prepared and their structures determined by magnetic moments, diffuse-reflectance and infrared spectra. The copper complexes have distorted octahedral or square-planar structures, and the nickel complex an octahedral structure. In these complexes the ligand coordinates to the metals through pyridine-N and amide-O atoms. The palladium complexes have square-planar structures with two unidentate paaH coordinating at the trans *position through pyridine-N atoms.*

Introduction

Previous studies have been made on the non-ionic and cationic complexes of pyridine-2-carboxamide,[1-5] pyridine-3-carboxamide[6] and pyrazine-2-carboxamide.[6] Pyridine-2-acetamide (abbreviation, paaH)(I) is different from these ligands by the lack of resonance between the pyridine ring and the amide group due to the presence of a CH_2 group in between. By this reason the hydrogen atom of the amide group may be difficult to dissociate and consequently only cationic complexes, $M(paaH)^{2+}$ and $M(paaH)_2^{2+}$ are expected to form. The present paper deals with the preparation and characterization of the cationic complexes of pyridine-2-acetamide by their magnetic moments, diffuse-reflectance and infrared spectra.



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Experimental Section

I. Preparations. 1. *The ligand, paaH.* Pyridine-2-acetic acid methyl ester was reacted with liquid ammonia in an autoclave at room temperature. The melting point of pyridine-2-acetamide recrystallized from benzene was 118-118.5°C, which was somewhat lower than the value, 122°C, of this amide prepared by different methods.[7]

2. *The 1:1 complexes*: α–$CuCl_2(paaH)$, β–$CuCl_2(paaH)$ and $CuBr_2(paaH)$. The two isomers of chloride complexes were obtained by adding an ethanol solution of $CuCl_2 . 2H_2O$ to a benzene solution of equimolecular amount of the ligand. Hot and cold benzene solutions were used to obtain α- and β-isomers, respectively.

The bromide complex was prepared by mixing equimolecular amounts of $CuBr_2$ and of the ligand dissolved in ethanol.

3. *The 1:2 complexes*: $CuCl_2(paaH)_2$, $CuBr_2(paaH)_2$, $Cu(ClO_4)_2(paaH)_2$ and $NiCl_2(paaH)_2 . 2H_2O$. These complexes were prepared by mixing one mole of the metal salt with two moles of the ligand. As solvents, ethanol and benzene were used for the first and second complexes and water was used for the third and fourth complexes.

4. *The palladium complexes*: $PdCl_2(paaH)_2$ and $PdBr_2(paaH)_2$. One mole of $PdCl_2$ or $PdBr_2$ dissolved in concentrated hydrochloric acid or hydrobromic acid was added to an aqueous solution of two moles of the ligand. Yellow crystals precipitated when the solution was neutralized with sodium hydroxide.

II. *Magnetic and spectroscopic measurements.* Magnetic moments were determined by the Gouy method at room temperature. The diffuse-reflectance spectra were obtained by a Hitachi EPU-2A spectrometer with the attachments. Magnesium oxide was used as the reference. The infrared spectra in the region 4000-700 cm^{-1} were measured with a JASCO DS-402G infrared spectromeater and those in the region 700-200 cm^{-1} with a Hitachi EPI-L infrared spectrometer in Nujol and HCB mulls and KBr discs.

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(5) A. Nawata, H. Iwasaki, and Y. Saito, *ibid.*, 515.
(6) M. Sekizaki and K. Yamasaki, *Revue de Chimie minérale*, *6*, 255 (1969).
(7) J. C. Godfrey, « Pyridine and its Derivatives », Part III, ed. by E. Klinsberg in the series of « The Chemistry of Heterocyclic Compounds », *Intersci.*, 1962, p. 472, and the references cited therein.

Table I. Analytical results (%)

	C		H		N		Metal	
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
paaH	61.94	61.75	6.07	5.92	20.35	20.58		
α—$CuCl_2$(paaH)	31.47	31.07	3.18	2.98	10.48	10.35	23.19	23.48
β—$CuCl_2$(paaH)	30.65	31.07	3.05	2.98	10.06	10.35	23.23	23.48
$CuBr_2$(paaH)	23.80	23.39	2.52	2.24	7.95	7.79	17.19	17.68
$CuCl_2(paaH)_2$	41.31	41.34	4.08	3.96	13.25	13.77	15.49	15.62
$CuBr_2(paaH)_2$	33.89	33.93	3.35	3.25	11.32	11.30	12.82	12.82
$Cu(ClO_4)_2(paaH)_2$	31.38	31.45	3.02	3.02	10.36	10.48	11.63	11.88
$NiCl_2(paaH)_2 . 2H_2O$ [a]	37.45	38.40	4.74	4.60	12.54	12.79	13.66	13.41
$PdCl_2(paaH)_2$	37.42	37.40	3.70	3.59	11.97	12.46	23.40	23.67
$PdBr_2(paaH)_2$	31.14	31.23	3.03	2.99	10.56	10.40	19.42	19.76

[a] H_2O: Found, 8.7%; Calcd., 8.23%.

Table II. Colors, magnetic moments, and absorption maxima of the diffuse-reflectance spectra

Complexes	Color	$\mu_{B.M.}$ (°C)	mμ(×1000 cm^{-1})		
α—$CuCl_2$(paaH)	dark green	1.86(28.0)	~1000(10.0)	625(16.0)	410(24.4)
β—$CuCl_2$(paaH)	blue green	1.86(29.5)	850(11.8) sh	700(14.3)	~400(25.0)
$CuBr_2$(paaH)	dark violet	1.82(24.5)	1150(8.7)	600(16.7) sh	530(18.9)
$CuCl_2(paaH)_2$	blue	1.85(19.5)	1000(10.0) sh	800(12.5)	
$CuBr_2(paaH)_2$	blue	1.86(29.0)		650(15.4)	
$Cu(ClO_4)_2(paaH)_2$	blue	1.86(29.0)		625(15.4)	
$NiCl_2(paaH)_2 . 2H_2O$	blue	3.24(29.5)	1000(10.0)	625(16.0)	390(25.5)
$PdCl_2(paaH)_2$	yellow	dia. (25.0)			~400(25.0)
$PdBr_2(paaH)_2$	yellow	dia. (25.0)			420(23.8)

sh, shoulder.

Results and Discussion

1. *General properties and magnetic moments.* The analytical data are listed in Table I, and the colors and magnetic moments in Table II. All the complexes except $CuBr_2$(paaH) which decomposes at 114-115°C are stable up to 150°C. The 1:1 complexes are easily decomposed in water and dimethylformamide, while the 1:2 complexes are soluble in these solvents except the palladium complexes. The magnetic moments are all normal.

2. *Diffuse-reflectance spectra.* The diffuse-reflectance spectra are shown in Figures 1, 2 and Table II.

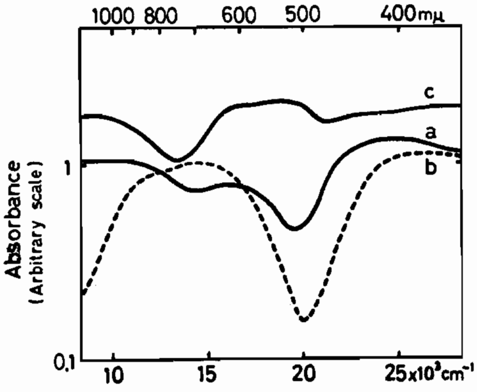

Figure 1. Diffuse-reflectance spectra of the 1:1 complexes. (a) α—$CuCl_2$(paaH); (b) β—$CuCl_2$(paaH); (c) $CuBr_2$(paaH).

In the solid state the copper complexes have generally distorted octahedral or square-planar structure of D_{4h} symmetry by the Jahn-Teller effect. Therefore, the copper complexes are expected to show three bands due to the transitions, ${}^2B_{1g}\rightarrow{}^2E_g$, ${}^2B_{1g}\rightarrow{}^2B_{2g}$ and ${}^2B_{1g}\rightarrow{}^2A_{1g}$. As the distortion becomes stronger these three bands seperate more clearly.[8] For the 1:1 complexes two distinct bands are found in the region longer than 600 mμ, which may be assigned to ${}^2B_{1g}\rightarrow{}^2B_{2g}$ and ${}^2B_{1g}\rightarrow{}^2A_{1g}$ (Figure 1), whereas the 1:2 complexes show only one broad band at about 700 mμ, indicating less distortion than the 1:1 complexes (Figure 2). Another band of the 1:1 complexes due to the transition, ${}^2B_{1g}\rightarrow{}^2E_g$, is presumably covered by the charge transfer band of coordinating halogens at about 400 mμ.

The nickel complex, $NiCl_2(paaH)_2 . 2H_2O$, shows a similar spectrum and magnetic moment as the previously reported $[Ni(H_2O)_2(piaH)_2]Cl_2$ [1] and [Ni-

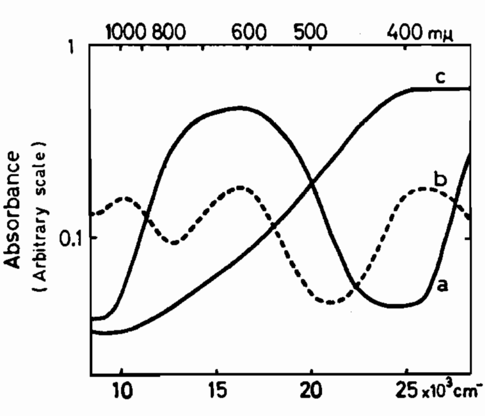

Figure 2. Diffuse-reflectance spectra of the 1:2 complexes. a) $Cu(ClO_4)_2(paaH)_2$; b) $NiCl_2(paaH)_2 . 2H_2O$; c) $PdCl_2(paaH)_2$.

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(8) D. W. Smith, *Inorg. Chem.*, 5, 2236 (1966).

Table III. Infrared spectra (cm^{-1})

	OCN stretch.				CH_2		CH_2 skel.	M–X	py-amide	M–N(py)
	antisym.	sym.	C=O i.p. and py o.p.	C=O o.p.	skel. def.	py o.p.	def.	stretch.	torsion	stretch.
paaH	1668 s	1402 s	655 s, 637 s, 592 s	548 s	481 m	405 s	343 m		248 m	
α–$CuCl_2$(paaH)	1648 s	1444 s	655 s, 623 s,	542 w, 534 w	483 w	428 s	380 w	323 s	270 s	225 m, 215 sh
β–$CuCl_2$(paaH)	1656 s	1446 s, 1433 s	697 s, 646 m, 615 s	535 m	484 w	428 s, 422 sh	369 s	320 s, 296 s	273 s	220 w
$CuBr_2$(paaH)	1644 s	1465 s	688 s, 635 s, 623 sh	534 m	472 w	430 s	397 s, 376 m	230 s	258 s	220 s
$CuCl_2(paaH)_2$	1654 s	1450 s, 1441 s	648 m, 625 w, 603 s	550 m, 541 m	481 w	431 s, 417 s	391 w, 380 w	351 w	278 w	237 w
$CuBr_2(paaH)_2$	1661 s	1454 s, 1438 s	649 m, 622 s	543 m	481 m	428 s	376 m	278 m	265 s	228 s
$Cu(ClO_4)_2(paaH)_2$ [a]	1651 s	1462 s	652 s, 620 sh	530 s	477 m	429 s	376 m	407 s	266 s	230 s
$NiCl_2(paaH)_2 . 2H_2O$	1657 s	1437 s	690 s, 649 s, 606 s	542 m	482 m	437 s	361 m		238 m	
$PdCl_2(paaH)_2$	1668 s	1418 s, 1391 s	665 s, 602 m	551 w	485 s	459 s	398 m, 377 w	350 s	283 s, 260 w	228 w
$PdBr_2(paaH)_2$	1650 s	1412 s, 1388 s	675 s, 630 s, 603 s	535 m	481 m	453 s	396 s, 372 m	261 s	293 m, 246 s	212 m

s, strong; m, moderate; w, weak; sh, shoulder; i.p.,in-plane deformation; o.p., out-of-plane deformation; skel.def., skeletal deformation; py, pyridine ring. [a] A strong band at 610 cm^{-1} is assigned to ClO_4 vibration.

$(H_2O)_2(pyaH)_2]Cl_2$ [6] where piaH and pyaH denote pyridine-2-carboxamide and pyrazine-2-carboxamide, respectively (Figure 2). Thus a similar octahedral structure with two water molecules in the *trans* positions is presumed for the nickel paaH complex.

The palladium complexes show a strong band in the near-ultraviolet region, which is usually observed for the square-planar palladium(II) complexes (Figure 2).

3. *Infrared spectra.* (1). *The 4000-700 cm^{-1} region.* In Table III are listed the frequencies of the two strong bands characteristic of the non-substituted amide group. The higher frequency band is assigned to the OCN antisymmetric stretching vibration mode and the lower one to the symmetric stretching vibration mode. For the copper and nickel complexes the OCN antisymmetric stretching band is observed at a little lower frequency region and the symmetric one at a higher frequency region than for the free ligand. These shifts are due to the coordination of the amide group through the oxygen atom as reported previously.[2] On the other hand, these two bands of $PdCl_2(paaH)_2$ and $PdBr_2(paaH)_2$ are observed almost at the same frequencies as those of the free ligand, indicating the non-coordination of the amide group.

(2). *The 700-200 cm^{-1} region.* The frequencies of the bands in the 700-200 cm^{-1} region are listed in Table III with some empirical assignments. The ligand itself shows a similar spectrum as pyridine-2-carboxamide except that the skeletal vibrations of CH_2 group are observed. For all the complexes except nickel, one or two strong bands are observed at 400-200 cm^{-1}, which are sensitive to anion substitution. These bands were not observed for the free ligand, and were assigned to the M–X stretching modes. According to the group theory, if the anions coordinate in the *trans* positions of a square-plane or an octahedron (D_{2h} symmetry), only one M–X stretching band (B_{2u} or B_{3u} type) is to be observed, whereas, in the case of *cis* coordination (C_{2v} symmetry) two M–X stretching bands (A_1 and B_1 types) are to be observed.[6] In Table III most of the complexes show only one M–X stretching band, indicating that anions coordinate in the *trans* positions to each other, but β–$CuCl_2$(paaH) shows two bands indicating *cis* coordination of two chloride ions.

The strong band observed at 407 cm^{-1} for $Cu(ClO_4)_2(paaH)_2$ may be assigned either to the Cu–O (oxygen of ClO_4) stretching, or to the Cl–O deformation mode, *i.e.* the E-band of C_{3v} symmetry.[9] Symmetry of the ClO_4 ion changed from T_d to C_{3v} by the strong distortion caused by coordination. The X-ray crystal analysis of this complex is now under investigation.

The nickel complex, $NiCl_2(paaH)_2 . 2H_2O$, which is presumed to have an octahedral structure shows a somewhat different spectrum from $[Ni(H_2O)_2(piaH)_2]Cl_2$. This may be due to the difference of the size of the chelate rings, namely the former has six-membered rings, while the latter five-membered rings. The fact that no Ni–Cl stretching band is observed corresponds to the presumed coordination of two water molecules instead of chloride ions. After the completion of this study, the papers by Shaw and Sutton on copper and nickel complexes of pyridine derivatives were published.[10] Among the complexes prepared by them the same complexes presented in this paper are found. $CuCl_2(paaH)_2$, $CuBr_2(paaH)_2$, $Cu(ClO_4)_2(paaH)_2$ and $NiCl_2(paaH)_2$. Most of the properties reported by them agree with our results, but following points are to be noted: 1. The absorption maximum of $CuCl_2(paaH)_2$ was found at 800 mμ, while they have reported it to be at 695 mμ. 2. They prepared the complexes $Cu(ClO_4)_2(paaH)_2 . 2H_2O$ and $NiCl_2(paaH)_2 . H_2O$, but the composition found by us are $Cu(ClO_4)_2(paaH)_2$ and $NiCl_2(paaH)_2 . 2H_2O$, respectively.

(9) K. Nakamoto, « Infrared Spectra of Inorganic and Coordination Compounds », John Wiley, 1963, p. 107.

(10) K. H. Shaw and G. J. Sutton, *Austral., J. Chem.*, *22*, 1835, 1841 (1969).