

SYNTHESIS AND CHARACTERIZATION OF SILVER(II) COMPLEXES OF SOME CARBONYL DERIVATIVES OF PYRIDINE

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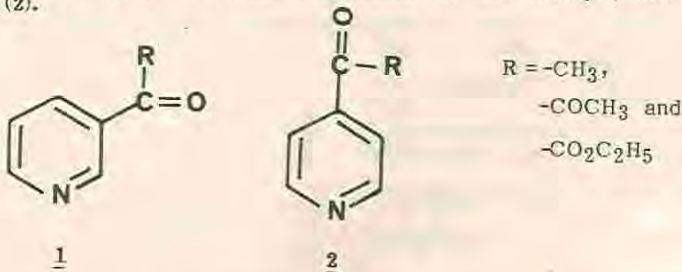
(Received May 7, 1991; revised September 2, 1991)

ABSTRACT. Silver(II) complexes of the type $[AgL_4]S_2O_8 \cdot H_2O$, where L is 3-, and 4-acetylpyridine, methyl-, and ethyl nicotinate and methyl-, and ethyl isonicotinate, have been prepared and characterized by their elemental analysis, electronic, infrared and EPR spectra and variable temperature magnetic susceptibility. Physical measurements have shown that the compounds studied contain the silver(II) ion most probably in a square planar arrangement or a tetragonal distorted octahedron. The magnetic susceptibility of the methyl nicotinate complex was found to follow the Curie-Weiss law in the range of 80-300 K

INTRODUCTION

The isolation of crystalline complexes of the unfamiliar divalent state of silver with pyridine, pyridine derivatives and pyridine carboxylic acids have been reported [1-15]. The pyridine and pyridine derivative complexes of silver(II) have the formula $[AgL_4] X_2$ where $X = \frac{1}{2} S_2O_8^{2-}$ or NO_3^- . In contrast to these complexes where complex cations are formed, the corresponding bis-pyridine monocarboxylic acid complexes of silver(II) are neutral (i.e. no counter ion is involved in the complex formation).

Silver(II) complexes of esters of pyridine monocarboxylic acids, however, have not yet been reported in the literature. This paper is concerned with the synthesis and characterization of such silver(II) complexes derived from 3-, and 4-acetylpyridines, methyl-, and ethyl nicotinates (1) and methyl-, and ethyl isonicotinates (2).



EXPERIMENTAL

Methyl nicotinate (Me-nic), ethyl nicotinate (Et-nic), 3-acetylpyridine (3-Acpy) and 4-acetylpyridine (4-Acpy) were obtained from BDH. Methyl-, and ethyl isonicotinates (Me-ison, and Et-ison, respectively) were prepared from isonicotinic acid (BDH) according to the method recommended by Vogel [16] for the preparation

of ethyl nicotinate.

Microanalysis of C, H and N were performed using a Perkin-Elmer 240 elemental analyzer. Silver was determined gravimetrically as AgCl after decomposing the complex by boiling with aqua-regia. Other physical measurements were carried out as described previously [17,18].

EPR spectra were recorded in the first derivative mode on a Varian E-109E X-band spectrometer with a Varian E-231-1 rectangular cavity operating at microwave frequency of ca 9.5 GHz. The frequency was measured with a Hewlett Packard 5342 A frequency counter. The g-values were calculated by measurement of the field shift relative to the external standard 1,1-diphenyl-2-picrylhydrazyl radical (DPPH) at $g = 2.0023$. A modulation frequency of 100 KHz was employed together with a modulation amplitude small enough to prevent lineshape distortion. Samples were placed in 4 mm OD super silica EPR tubes and connected to a vacuum line.

The least squares fitting of the magnetic susceptibility data was carried out on IBM PC/XT computer using SPSS/PC statistical package for Curie-Weiss law.

Preparation of the silver(II) complexes. The complexes were prepared by adding about 25 mmol of the ligand to about 5 mmol silver nitrate dissolved in 30 cm³ of distilled water. In some cases a white precipitate of silver(I) complex was formed immediately. To this mixture an excess amount of solid K₂S₂O₈ was added and the final mixture allowed to stand over a variable time, from several minutes in case of 3-acetylpyridine to overnight in case of methyl nicotinate, to produce the complex as a microcrystalline powder. In case of 4-acetylpyridine a continuous stirring for several hours followed by allowing the solution to stand over two days in presence of excess of potassium persulphate is required. The complexes were filtered off, washed with distilled water and dried using a vacuum pump. Addition of aqueous solution of K₂S₂O₈ instead of solid gives a small yield (30-40% to >50% respectively).

Table 1 summarizes the elemental analysis results and some other physical properties of the resulting complexes.

Table 1. Analytical data of complexes.

Complex	Color	Product %	Analysis : Fund calc.			
			C	H	N	Ag
[Ag(Me-nic) ₄]S ₂ O ₈ .H ₂ O	brownish red	60	38.42	3.62	6.24	12.80
			38.81	3.46	6.46	12.45
[Ag(Et-nic) ₄]S ₂ O ₈ .H ₂ O	orange red	50	40.98	4.26	6.22	11.70
			41.66	4.15	6.67	11.69
[Ag(Me-ison) ₄]S ₂ O ₈ .H ₂ O	red crystals	65	39.00	3.52	6.62	12.50
			38.81	3.46	6.46	12.45
[Ag(Et-ison) ₄]S ₂ O ₈ .H ₂ O	orange red	60	41.88	4.46	6.50	11.80
			41.66	4.15	6.07	11.69
[Ag(3-Acpy) ₄]S ₂ O ₈ .H ₂ O	yellowish orange	80	42.21	3.80	7.08	13.28
			41.90	3.77	6.98	13.44
[Ag(4-Acpy) ₄]S ₂ O ₈ .H ₂ O	red	50	41.80	3.52	6.52	13.68
			41.90	3.77	6.98	13.44

Abbreviations: Et-nic = ethyl nicotinate, Me-nic = methyl nicotinate,
Et-ison = ethyl isonicotinate, Me-ison = methyl isonicotinate,
Acpy = acetyl pyridine.

RESULTS AND DISCUSSION

Oxidation of silver(I) in presence of methyl and ethyl esters of nicotinic or isonicotinic acids as well as 3-, and 4-acetylpyridine results in the isolation of polycrystalline compounds of tetrakis-(amine) silver(II) persulphate complexes. All complexes are hydrated, which is not surprising in view of the media they were obtained from and what is known about other silver(II) complexes [1].

All compounds are insoluble in both polar and non-polar solvents. They are generally less stable in air when compared with the parent acid-silver(II) complexes.

Infrared spectra. Comparison of the infrared spectra of the title complexes with those of free ligands show that the carbonyl stretching vibrations of all 3-, and 4-carbonyl ligands under consideration are not affected by complexation with silver(II). For these ligands the C-C, C-N ring vibrations are shifted to higher frequencies in the spectra of complexes, suggesting their coordination via the nitrogen atom only. Bands around $3500-3200\text{ cm}^{-1}$ and 1650 cm^{-1} are assigned [19] to lattice water. The water molecules are involved in H-bond formation as indicated by the broadness of the former medium to strong band. The absorption bands due to the persulphate groups appeared in the regions $1300-1240\text{ cm}^{-1}$ (very strong and broad), $1150-1110\text{ cm}^{-1}$ (very strong) and $690-550\text{ cm}^{-1}$ for all complexes suggest ionic $\text{S}_2\text{O}_8^{2-}$ groups [20]. The shape and position of these bands are very similar to those observed in the spectrum of a freshly prepared $[\text{Ag}(\text{py})_4]\text{S}_2\text{O}_8$ complex known to contain ionic persulphate group [1].

Electronic spectra. The results of electronic spectra of the complexes measured as solids milled in nujol are given in Table 2, and compared to published data on silver(II) complexes of other related ligands [5,7,10].

Table 2. Electronic spectra and room temperature magnetic moments.

Complex	Maximum absorption (cm^{-1})	μ_{eff} (BM)	Reference
$[\text{Ag}(\text{Me-nic})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$	25600, 19600 (sh)	1.88	This work
$[\text{Ag}(\text{Et-nic})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$	25600, 19600 (sh)	1.80	This work
$[\text{Ag}(\text{Me-ison})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$	28700, 21300 (sh)	1.85	This work
$[\text{Ag}(\text{Et-ison})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$	27800, 21300 (sh)	1.79	This work
$[\text{Ag}(3\text{-Acpy})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$	32200-18200 (v br)	1.82	This work
$[\text{Ag}(4\text{-Acpy})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$	27000	1.92	This work
$[\text{Ag}(\text{py})_4]\text{S}_2\text{O}_8$	22000		6
$[\text{Ag}(4\text{-pic})_4]\text{S}_2\text{O}_8$	27000		7
$[\text{Ag}(\text{picolate})_2]$	30000, 24500		10
$[\text{Ag}(\text{quin-II})_2] \cdot 2\text{H}_2\text{O}$	30200, 22800		10

picolate H = picolinic acid, pic = picoline;

quin H₂ = quinolinic acid (pyridine-2,3-dicarboxylic acid).

Even though a square planar configuration should result in at least three bands in the range of d-d transitions, resolution is frequently poor, in particular when dealing with dull or diffuse reflectance spectra. Estimation of ligand field parameters using curve-resolving procedures has been carried out [21,22], however, where only a broad asymmetrical band is encountered, rather than shoulders, data obtained may not be very reliable. In general the occurrence of a broad band at $25,000-22,000\text{ cm}^{-1}$ is regarded as evidence for a square planar arrangement in coordination complexes of silver(II) [1,10,11]. Electronic spectral data given in Table 2 led us to conclude that similar stereochemistry exists for these complexes. However, a tetragonally distorted octahedral geometry can not be

Table 3. EPR spectral data of silver(II) complexes.

Complex	Medium	T (K)	g ₁ or (g ₁)	g ₂	g ₃ (g ₁₁)	G	μ_{eff}^*	Reference
[Ag(Me-ison) ₄]S ₂ O ₈ ·H ₂ O	solid	284	2.053		2.192	3.62	1.81	This work
[Ag(Et-ison) ₄]S ₂ O ₈ ·H ₂ O	solid		2.053		2.192	3.62	1.81	This work
[Ag(Me-nic) ₄]S ₂ O ₈ ·H ₂ O	solid	295	2.089		2.229	2.57	1.84	This work
[Ag(Et-nic) ₄]S ₂ O ₈ ·H ₂ O	solid*	298	2.093		2.259	2.78	1.86	This work
[Ag(Me-nic) ₄]S ₂ O ₈ ·H ₂ O	solid	298	2.048		2.489	3.94	1.81	This work
[Ag(Et-nic) ₄]S ₂ O ₈ ·H ₂ O	solid	298	2.020	2.084	2.229	4.40	1.83	This work
[Ag(py) ₄]S ₂ O ₈	solid	110	1.990	2.077	2.222	6.60	1.81	This work
	dil. with		2.040		2.180	4.50		[5]
	[Cd(py) ₄](S ₂ O ₈)		2.060		2.160	2.66		[13]
			2.420		2.214	5.09		[27]
	solid		2.049	2.098	2.148	2.01		[13]
[Ag(picolate) ₂]	solid		2.044	2.089	2.158	2.39		[26]
	solid		2.040		2.180	4.50		[14]
	solid		2.044	2.072	2.224	4.20		[13]
[Ag(3- Δ cpy) ₄]S ₂ O ₈ ·H ₂ O	solid	299	<g>	2.079			1.80	This work
[Ag(nicotinate) ₂]	solid	110	<g>	2.052			1.77	This work
	solid	289	<g>	2.080				[15]

μ_{eff}^* calculated from $\mu_{\text{eff}} = g_0[S(S+1)]^{1/2}$.

* Spectra of other different samples.

ruled out since a broad band at approximately $22,800\text{ cm}^{-1}$ for bis(pyridine-2,3-dicarboxylate)silver(II) dihydrate had been attributed to unresolved d-d bands [10]. X-ray structural analysis of this complex has revealed a highly tetragonally distorted octahedron, if one takes into consideration the long axial Ag-O bands of 2.9 \AA [23]. This latter geometry may be attained in complexes under consideration by a weak interaction between the silver atom and the carbonyl oxygen of the 3-, or 4-position of neighbouring molecules. Such a weak interaction may not be detected by the infrared spectra. Very recently [24], X-ray structural analyses have shown that ethyl-, and methyl quinaldates coordinate copper(II) ion via their carbonyl groups as well as the heterocyclic nitrogen, although the $\nu_{\text{C=O}}$ bands were not influenced by coordination [25].

Magnetic properties. The room temperature magnetic moment given in Table 3, fall in the vicinity of the spin-only value of 1.73 B.M. expected for a silver(II) ion with $4d^9$ electronic configuration. These values which are very close to those reported for silver(II) complexes of pyridine [3,24] picolines [7] picolinic acid [9,10] and other related ligands [3,10,11] possessing square planar or distorted octahedral structures, may rule out a tetrahedral arrangement for complexes under consideration. For this latter arrangement the magnetic moments should be in excess of 2.0 B.M., and be markedly dependent upon temperature [10].

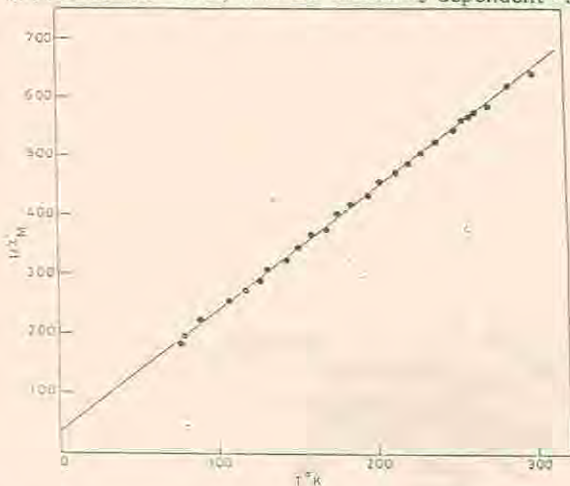


Fig. 1. Temperature dependence of the inverse susceptibility of $[\text{Ag}(\text{Me-nic})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$. Experimental data are depicted as open circles and the best fit to the Curie-Weiss expression ($\theta = 16.55$) is shown as the full line.

The magnetic susceptibilities of the $[\text{Ag}(\text{Me-nic})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$ complex were measured in the range of 77–300 K, and data were found to fit the Curie-Weiss law with calculated Weiss constant of 16.55 K. A plot of the inverse molar susceptibility vs temperature along with the best-fit Curie-Weiss curve is presented in Fig. 1. The effective magnetic moments, calculated from the relationship $\mu_{\text{eff}} = 2.83[X_M(T-\theta)]^{1/2}$, varies from 1.88 B.M. at 300 K to 1.60 B.M. at 77 K. In fact, all the silver(II) complexes studied, with the exception of those of nicotinic acid [15] and pyrazine [25] which are antiferromagnetics, exhibited Curie or Curie-Weiss behaviour with $\theta \leq 10$ K. Thus the value of ≈ 17 K which is a little higher than those for other Silver(II) complexes may indicate the existence of some magnetic interactions in the methyl nicotinate complex.

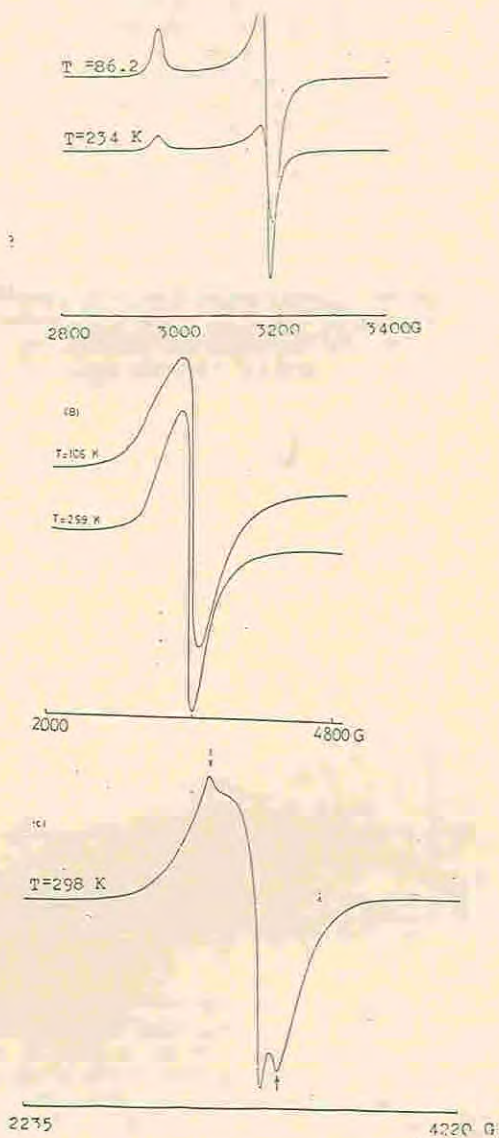


Fig. 2. EPR spectra of polycrystalline solid complexes: (A) $[\text{Ag}(\text{Et-ison})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$; (B) $[\text{Ag}(3\text{-Acpy})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$; (C) $[\text{Ag}(\text{Et-nic})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$.

EPR spectra. Electron spin resonance spectra on polycrystalline powders are obtained at room and liquid nitrogen temperatures. The g values are listed in Table 3 together with relevant literature values.

No silver or nitrogen hyperfine could be recorded in spectra of solids, as have been found for silver(II) complexes of other related ligands. However, a broad isotropic spectrum is found for $[\text{Ag}(\text{3-AcPy})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$. This spectrum is very close to that reported for the antiferromagnetic silver(II)-nicotinic acid complex possessing a polymeric linear chain structure [15]. Therefore, and as discussed for similar situation in complexes of copper(II) [28] a grossly misaligned set of tetragonals seems to be a more plausible explanation than regular octahedral or tetrahedral coordination around Ag^{2+} .

For the remaining silver(II) complexes, except that of ethyl nicotinate, spectra of two g -values type were recorded. These spectra (Fig.2) are typically characterizing axial symmetry. $[\text{Ag}(\text{Et-nic})_4]\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$ has a three g -values spectrum. The values obtained for g_1 components in all cases indicate a $d_{x^2-y^2}$ (${}^2B_{1g}$) ground state. The g values listed in Table 3 are in good agreement with previous work on complexes containing the $[\text{AgL}_4]^{2+}$ ion where L is pyridine [5,13,26,27] or 4-picoline [27].

The values of a parameter calculated from $G = (g_{11} - 2)/(g_1 - 2)$ and $G = (g_3 - 2)/(g_1 - 2)$ [where $g_1 = \frac{1}{2}(g_1 + g_2)$] for two and three g -values spectra, respectively, are given in Table 3. Values of G around 3.5-5.0 observed for silver(II) complexes of methyl isonicotinate and ethyl nicotinate are indicative of magnetically dilute compounds [28,29]. In the case of the ethyl nicotinate complexes a value of 2.57 observed for G may indicate an appreciable magnetic interaction. For the methyl nicotinate complex the spectra of two different samples were recorded giving rise to different g and G parameters. The G values of 2.78 and 3.94 are indicative of magnetically concentrated and diluted respectively. The former value is consistent with the Weiss constant value obtained from magnetic susceptibility measurements. In fact a similar situation was reported for $[\text{Ag}(\text{pyridine})_4]\text{S}_2\text{O}_8$ where different two and three g -values spectra were reported [3,13,26,27]. However, as this complex is known to possess a square planar geometry, Buch [5] suggested that the spectrum belongs to a rhombic g -tensor may arise from exchange coupled pairs of Ag^{2+} ions in their triplet states. While this interpretation is in contradiction with some magnetic susceptibility measurements [4] indicating Curie's law dependence down to 1.6 K, it agrees with previous measurements showing antiferromagnetic behaviour with a Weiss constant $\theta = -26$ °K [30]. In the case of silver(II) compounds under consideration the EPR data are consistent with electronic spectral results suggesting square planar or tetragonally distorted octahedral structures, and good agreement is observed between calculated magnetic moments (Table 3) and experimental values (Table 2).

ACKNOWLEDGEMENT

The authors are thankful to Dr. A. Ellaboudy, Department of Chemistry, Michigan State University, for EPR measurements.

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