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HETEROCYCLIC AND MACROCYCLIC AMINE COMPLEXES OF SILVER(II) AND SILVER(III)

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CONTENTS

ABBREVIATIONS

Table 1

py	pyridine
bipy	2,2′-bipyridine
phen	1,10-phenonthroline
terpy	2,2′,2″-terpyridine
pic	picolinate ion

nic	nicotinate ion
isonic	isonicotinate ion
$quinH_2$	quinolinic acid
$cinchH_2$	cinchomeronic acid
$isocinchH_2$	isocinchomeronic acid
$lutH_2$	lutidinic acid
$dipicH_2$	dipicolinic acid
isoquin-1-COO	isoquinoline-1-carboxylate ion
pyz	pyrazine
pyzCOO	pyrazine-2-carboxylate ion
PPDE and MPDE	see substituted porphyrins in Fig. 8

Table 2

$(iso\text{-}C_3H_7)_2NCS_2$	N,N-diisopropyl-dithiocarbamate ion
DPME and EPDE	see Fig. 8

Table 3

OEP, TPP and TPPS	see Fig. 8

Table 5

enbisbig	ethylenebis(biguanide)

A. INTRODUCTION

Bi- and trivalent silver ions are rather unstable due to the powerful oxidizing nature of these ions in solution. This is reflected by the fact that only very electronegative groups such as fluorine form simple binary compounds (e.g. AgF_2) with Ag(II). Similarly, species such as the periodates bind with Ag(III) to form complex compounds. These unfamiliar oxidation states of silver are strongly stabilized by coordination with organic ligands, most notably the nitrogen-containing heterocycles such as the pyridines, polypyridines and derivatives, and the macrocycles. Here we review the chemistry of these silver(II) and silver(III) complexes with particular emphasis on recent structural elucidation and bonding studies on these complexes. Although previous review articles [1,2] (bibliographies included in these reviews are complete only to Dec. 1961) gave account of compounds of silver(II) and silver(III), treatment of the subject was limited mostly to methods of preparation and magnetic susceptibility measurements. With recent additional structural information from X-ray studies and data from electron paramagnetic resonance, X-ray photo-electron and UV-visible and diffuse reflectance spectroscopy, much more is known about the chemistry of bi- and trivalent silver complexes. This review is extended to include complexes of macrocyclic ligands such as the porphyrins and tetraaza ligands.

B. ORGANIC COMPLEXES OF SILVER(II)

Generally, one of the following procedures can be used to prepare heterocyclic amine—silver(II) complexes. These complexes normally exhibit four coordination. Recently, however, hexa-coordinate complexes have also been prepared using method (i) described below.

(i) Ammonium or potassium persulfate oxidation of a cold aqueous silver nitrate solution with excess ligand present. The low solubility of these salts in aqueous solution allows the easy isolation of the compounds usually as the persulfate salts. This is perhaps the most common method used for the following ligands: pyridines, polypyridines, *o*-phenanthroline, pyridine-monocarboxylic, dicarboxylic, and tricarboxylic acids. Replacement of the persulfate ions with nitrate, bisulfate, perchlorate, or chlorate ions has been achieved.

(ii) Anodic oxidation of a solution of silver nitrate containing an excess of ligand in a divided cell.

(iii) Oxidation of the corresponding silver(I)-complex with a powerful oxidizing agent such as ozone provided the ligand is not attacked by the oxidizing agent. In one case, silver(II) oxide dissolved in concentrated nitric acid mixed with a solution containing the ligand (bipy or *o*-phen) yielded the described product.

(iv) With certain free porphyrin bases [3] and tetraaze ligands [4], the silver(II)-complexes could be obtained directly from the silver(I) and the macrocyclic amine solution. Apparently a disproportionation reaction occurs when silver(I) salts are mixed with the macrocyclic amines.

$$2\,Ag^+ + L = AgL^{2+} + Ag^0 \qquad (1)$$

The solid compounds of many coordinated silver(II)-complexes [1] are highly crystalline powders and may vary in color from yellow to dark red. They are usually hydrated and are sparingly soluble in water. Many of these compounds are powerful oxidizing agents and have been employed in organic synthesis work in the oxidation of alcohols, aldehydes, amines [5], and decarboxylation of acids [6]. Invariably, magnetic susceptibility measurements on these $4d^9$ systems show an effective magnetic moment per silver atom near ~1.8 BM, strongly suggesting quenched orbital angular momentum and spin-only paramagnetism. Magnetic data for complexes of silver(II) are listed in Table 1.

TABLE 1

Magnetic susceptibilities, effective magnetic moments, and Curie—Weiss constants of Ag(II) complex compounds at ~298 K

Ag(II) compounds	μ_{eff} (BM)	Curie—Weiss constant (°K)	Ref.
$Agpy_4(S_2O_8)$	1.71—1.78	(26 ?)	88,31,89,90
$Ag(3\text{-}Me\text{-}py)_4(S_2O_8)$	1.74		15
$Ag(4\text{-}Me\text{-}py)_4(S_2O_8)$	1.74		15
$[Ag(bipy)_2]X_2$			
X: $1/2\ S_2O_8^{2-}$	1.82		88,90
NO_3^-	2.12		89
NO_3^-	2.12		21
ClO_3^-	2.08		89
ClO_4^-	2.29		89
$F_3CSO_3^-$			21
$Agbipy_2(S_2O_8) \cdot H_2O$	1.94		91
$Ag_2bipy_5(S_2O_8)_2$	2.04		89
$Agphen_2(S_2O_8)$	1.84		91
$[Ag(terpy)(ClO_3)]ClO_3$	1.85		91
$Ag(terpy)(S_2O_8) \cdot H_2O$	1.85		35
$[Ag(terpy)_2]S_2O_8 \cdot 3\ H_2O$	1.87		35
$Ag(pic)_2$	1.83	+10	38,36
$Ag(nic)_2$	1.67, 1.74	+52 (+42)	38,36,45 (43)
$Ag(isonic)_2 \cdot H_2O$	1.81, 1.60	+10	38,36
$Ag(quinH)_2 \cdot 2\ H_2O$	1.80, 1.74	+4	38,45
$Ag(cinchH)_2 \cdot H_2O$	1.79, 1.74	+4	38,45
$Ag(isocinhH)_2$	1.78, 1.71	+9	38,45
$Ag(lutH)_2 \cdot 2\ H_2O$	1.81, 1.64		50,45
$Ag(dipic)(dipicH_2) \cdot 4\ H_2O$	1.74 (1.75)	0	38,45
$\cdot H_2O$	1.75		38
$Ag(py\text{-}2,4,6\text{-}(COO)_3)$ black	1.82		56
brown	1.83		56
$Ag(py\text{-}2,4,5\text{-}(COO)_3)$	1.73		56
$Ag(dipic)(terpy) \cdot 4\ H_2O$	2.14		51
$Ag(dipic)(bipy) \cdot 3\ H_2O$	1.88		51
$Ag(dipic)(phen) \cdot 7/2\ H_2O$	1.69		51
$Ag(dipicH)(terpy)(S_2O_8)_{0.5} \cdot 2\ H_2O$	1.82		51
$Ag(pic)(terpy)(S_2O_8)_{0.5} \cdot 2\ H_2O$	2.04		51
$Ag(quinH)(terpy)(S_2O_8)_{0.5}$	1.82		51
$Ag(lutH)(terpy)(S_2O_8)_{0.5} \cdot H_2O$	1.89		51
$Ag(isocinchH)(terpy)(S_2O_8)_{0.5}$	1.91		51
$Ag(isoquin\text{-}1\text{-}COO)_2$	1.81		50
$Ag(pyz)_2S_2O_8$	1.61	+84	52
$Ag(pyzCOO)_2$	1.79	+8	52
$Ag(I)_2Ag(II)(pyz\text{-}2,3\text{-}(COO)_2)_2$	1.76	+2	52
AgPPDE	1.87		92
AgMPDE	~0.8		66
(Ia) [a]	2.2		4
(IIa) [a]	1.95		4
(III) [a]	1.81		4
(IV) [a]	1.96		4

[a] See Fig. 10.

(i) Pyridine and polypyridine complexes of Ag(II)

[Ag(py)$_4$]X$_2$

This was first prepared as a persulfate salt (X = 1/2 $S_2O_8^{2-}$) by Barbieri [7]. The corresponding nitrate salt (X = NO_3^-) can also be prepared by anodic oxidation. These compounds are orange or orange-red crystals depending on

TABLE 2

Principal values of the g-tensor from EPR studies of Ag(II) complex compounds

Ag(II) compound	Medium	g_x	g_y	g_z	Ref.
Agpy(S_2O_8)	Diluted with Cdpy$_4$(S_2O_8)	2.04 [a]		2.18	12,8,13
	Diluted with Cdpy$_4$(S_2O_8)	2.06 [a]		2.16	9
	Solid	2.049	2.098	2.148	10
	Solid	2.044	2.089	2.158	11
trans-Agpy$_2$(NO_3)$_2$	Frozen HNO_3 solution, 77 K	2.050 [a]		2.178	16
	Solid, 77 K	2.035	2.062	2.187	16
Agbipy$_2$(S_2O_8)	Solid	2.032 [a]		2.164	10
	Aq. solution	2.045 [a]		2.129	21
	Frozen HNO_3 solution, 77 K	2.047 [a]		2.210	29
	Solid, 77 K	2.047 [a]		2.184	29
Agbipy$_2$(NO_3)$_2$	Solid	2.037	2.047	2.168	10
Agbipy$_2$(ClO_4)$_2$	Solid	2.045 [a]		2.169	10
Agbipy$_2$(ClO_3)$_2$	Solid	2.034	2.065	2.172	10
Ag$_2$bipy$_5$(S_2O_8)$_2$	Solid	2.040	2.056	2.176	10
Agphen$_2$(S_2O_8)	Solid	2.046		2.168	10
Ag(pic)$_2$	Solid	2.04 [a]		2.18	32
	Solid	2.044	2.072	2.244	10
Ag(nic)$_2$	Solid	$\langle g \rangle$ =	2.05		43
Ag[(iso-C_3H_7)$_2$NCS$_2$]$_2$	Frozen C_6H_6 solvent	2.011 [a]		2.035	60
(Ia)	Polycrystalline sample at room temperature	2.058 [a]		2.11	4
(IIa)	Polycrystalline sample at room temperature	2.038 [a]		2.095	4
(III)	Polycrystalline sample at room temperature	2.07 [a]		1.997	4
Ag(DPDE)	CCl_4 ambient temp.	2.03 [a]		2.10	68
Ag(MPDE)	Acetone (77 K) or 1-chloronaphthalene (77 K)	2.03 [a]		2.107	69
Ag(DPDE)	Acetone (77 K) or 1-chloronaphthalene (77 K)	2.03 [a]		2.106	69
Ag(EPDE)	Acetone (77 K) or 1-chloronaphthalene (77 K)	2.03 [a]		2.104–2.107	69
Ag(phthalocyanine)	Polycrystalline	2.017 [a]		2.093	26
	77 K, 1-chloronaphthalene	2.017 [a]		2.093	26

[a] Symmetric magnetic complex $g_\perp = g_x = g_y$ (only g_x value will be listed) and $g_\parallel = g_z$.

the anions. EPR studies of diluted and undiluted $[Ag(py)_4]S_2O_8$ are conflicting. Gijsman et al. [8] found axial symmetry for the diluted salt (Ag : Cd = 1 : 20.3) with $g_\perp(g_x = g_y) = 2.04$ and $g_\parallel(g_z) = 2.18$ very close to those reported by Garif'yanov et al. [9]. Apparently conflicting results obtained by McMillan and Smaller [10] and Johnston and Hecht [11] on pure solid $[Ag(py)_4]S_2O_8$ disclosed strong g-anisotropies (Table 2). In all instances (except ref. 9) no hyperfine features have been reported. However, Buch's [12] EPR studies at 77° with polycrystalline solid solutions of $[Ag(py)_4]$-S_2O_8 and $[Cd(py)_4]S_2O_8$ at Ag : Cd = 1 : 100 reveal hyperfine structure and axial symmetry with earlier quoted g values [8]. With increasing Ag concentration the hyperfine structure is obliterated by line broadening and gives a spectrum which can be interpreted with a rhombic g-tensor as reported in ref. 10. Hecht and Frazier [13], restudied the system and obtained both types of spectra. They offer a tenable explanation that the removal of axial symmetry is very likely due to distortions of the complex ions themselves in the particular way they are packed in the lattice. However, in the diluted solid solution, it might be argued that $Ag(py)_4^{2+}$ prefers the square planar configuration in a cadmium complex environment, which will likely be tetrahedral. The square planar configuration for $Ag(py)_4^{2+}$ is supported by electronic absorption maximum data, ~22.0 [13] and 20.4 kK [14], of the persulfate salts. The d—d band is at an energy much too large for the corresponding tetrahedral complex which is expected to absorb at 10—12 kK. The silver hyperfine coupling constants calculated assuming the pyridine ligands in a square planar arrangement are as follows

$A_{\parallel Ag} = 42.4 \qquad A_{\perp Ag} = 19.2 \times 10^{-4}\ cm^{-1}$ [13]

Complexes of silver(II) with 3- or 4-methylpyridine have been prepared and magnetic moments reported indicate spin-only paramagnetism [15].

trans-$Ag(py)_2(NO_3)_2$

The EPR spectrum of $Ag(py)_2^{2+}$ in frozen nitric acid solution at 77° exhibits silver hyperfine and nitrogen super-hyperfine structures [16]. The model adopted by the authors is that of a silver ion coordinated to two nitrogen atoms opposite to each other along the z axis. The axial symmetry determined for the frozen acid solution yielded $g_\perp = 2.050 \pm 0.001$ and $g_\parallel = 2.178 \pm 0.001$. However, a slight orthorhombic symmetry with g-anisotropy was obtained for the polycrystalline solid (Table 2). The experimental values are consistent with the silver d_{z^2} orbital occupied by the hole in an oblate tetragonal octahedron. The hole is partially transferred to a nitrogen hybrid orbital. The C—N—C angle calculated is 131°, in fairly good agreement with an independently estimated value of 126° [16].

$[Ag(bipy)_2]X_2$

Red-brown crystals of bis(2,2'-bipyridyl) silver(II) salts have been prepared by persulfate, anodic and ozone oxidation with $X = 1/2\ S_2O_8^{2-}$,

HSO_4^-, NO_3^-, ClO_3^-, or ClO_4^- [17—20]. The nitrate salt decomposes at 174°, whereas the recently reported $F_3CSO_3^-$ salt decomposes at 200—210°. Thorpe and Kochi [21] have confirmed that these complexes contain two bipyridine ligands and not three. A powerful oxidant, the redox potential for $Ag(bipy)_2^{2+}/Ag(bipy)_2^+$ has been reported to be 1.453 V [22] with a temperature coefficient of 0.0012 V deg^{-1} [23]. Bulk magnetic susceptibility measurements for compounds with $X = NO_3^-$, ClO_3^-, ClO_4^-, and $[Ag_2(bipy)_5](S_2O_8)_2$ have revealed magnetic moments at 2.04—2.29 BM, higher than the orbitally quenched spin-only value for the d^9 system. All of these solids show strong *g*-anisotropies (Table 2). The electronic spectrum of aqueous $Ag(bipy)_2^{2+}$ shows an absorption maximum at 22 kK with several values reported for the extinction coefficients; 2160 ± 40 [24], 1980 [14] and 1600 [25] l mol^{-1} cm^{-1}. Banerjee and Basu [14] report the *d—d* band for this complex composed of three transitions expected from a d^9 square plane structure.

EPR of an aqueous solution of $[Ag(bipy)_2](NO_3)_2$ shows a partially resolved hyperfine structure of eleven lines equally spaced in an almost isotropic spectrum [21]. This allows a direct comparison with Ag(II) constrained in the cavity of porphyrin [26] and does suggest that in aqueous solution the $Ag(bipy)_2^{2+}$ must be coordinated to the four pyridyl nitrogen atoms of the two bipyridine ligands.

A recent X-ray diffraction study on a $[Ag(bipy)_2](NO_3)_2 \cdot H_2O$ single crystal has shown that the silver atom is strongly coordinated to all four nitrogen atoms of the bipyridines with two bridging NO_3^- groups at 2.78 and 2.82 Å completing the coordination [27] (Fig. 1). One of the bipyridine ligands is planar and the other non-planar. A dihedral angle of 7° between planar individual pyridine groups is observed. The plane described by the silver nuclei and the nitrogen atoms of the non-planar unit makes a dihedral angle of 28° with the planar unit. The N—Ag—N bond angles are ~77°. Nitrate bridging has also been shown in the dinitratobipyridyl-silver(II) [28].

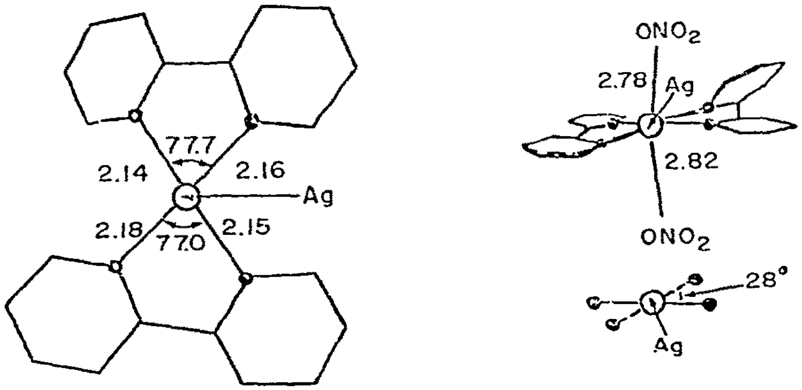


Fig. 1. Structure of bis(2,2'-bipyridyl)silver(II) nitrate monohydrate.

EPR studies of Halpern et al. [29] of solid and frozen nitric acid solution of $[Ag(bipy)_2](NO_3)_2$ have been interpreted with Ag(II) coordinated to four nitrogen atoms in the solid. Meanwhile, the solution's hyperfine and super-hyperfine structures also show quite conclusively Ag(II) coordination with only two N atoms. The square planar model adopted involves coordination with two pyridyl nitrogens and two solvent oxygens in alternate sequence. This alternate arrangement on the square plane is quite different from the *trans* arrangement along the z axis of the $[Ag(py)_2](NO_3)_2$. The square planar configuration is supported by the silver hyperfine coupling constants $|A_{\parallel}(Ag)| = 42.2 \pm 0.1$ G, $|A_{\perp}(Ag)| = 26.0 \pm 0.16$ G. The lowest energy level for the hole in the d shell is $d_{x^2-y^2}$ and not in the d_{z^2} orbital as in an oblate octahedron. The hole has been determined to be quite highly delocalized.

The EPR spectrum of $[Ag(bipy)_2](NO_3)_2$ in aqueous solution shows coordination with four nitrogen atoms [21], whereas in frozen HNO_3 at 77 K only two N atoms are bonded [29]. This discrepancy could be due to protonation of a bipyridine and dissociation of the ligand.

$$Ag^{II}(bipy)_2^{2+} + H^+ = Ag^{II}(bipy)^{2+} + bipyH^+ \tag{2}$$

However, such reaction would produce an $Ag(II)(bipy)^{2+}$ complex of two nitrogens at *cis* positions in the square plane, contrary to the *trans* model adopted by Halpern et al. [29]. A recent kinetic study on the reduction of $Ag(bipy)_2^{2+}$ by H_2O_2 in aqueous solution shows a sigmoidal pH kinetic dependence which can be explained with the incorporation of the following reaction [24].

$$Ag(II)(bipy)_2^{2+} + 2\,H^+ = Ag(II)(Hbipy)_2^{4+} \tag{3}$$

The protonated complex subsequently undergoes reduction by H_2O_2. Such a species would probably account for the model proposed for the complex in the frozen acid solution with coordination to two nitrogen atoms alternate with two solvent oxygens [29].

$[Ag(phen)_2]X_2$

Several methods have been used to prepare this complex with X = 1/2 $S_2O_8^{2-}$, NO_3^-, ClO_3^-, or HSO_4^- [30,31]. The red-brown salt is very insoluble in water, much more so than the bis(bipyridyl)silver(II). EPR studies indicate axial symmetry with $g_{\parallel} = 2.168$ and $g_{\perp} = 2.04$ [32]. It seems likely that the hole in the 4d subshell is delocalized to the surrounding N atoms. Electronic spectra show strong absorption at 350—400 nm, an indication of a d^9 square planar structure [33]. We have examined the UV spectrum of an aqueous solution of $Ag(phen)_2^{2+}$ in excess $K_2S_2O_8$ and found two shoulders at 322 and 306 nm. The redox potential has been reported to be 65 mV less than the corresponding $Ag(bipy)_2^{2+}/Ag(bipy)_2^{+}$ couple [34].

$[Ag(terpy)_2]S_2O_8 \cdot 3\,H_2O$

Previous preparation always yielded the mono-2,2′,2″-terpyridine complex of silver(II), $Ag(terpy)S_2O_8 \cdot H_2O$ or [Ag(terpy)X]X, where X =

NO_3^-, ClO_3^-, ClO_4^- [20]. Recently, the dark brown bis-complex, the titled compound, has been prepared with excess ligand concentration (molar ratio L : Ag = 2.5 : 1) [35]. The IR spectra of $Ag(terpy)S_2O_8 \cdot H_2O$ and the bis-complex show characteristic water bands centered at 3360 and 3250 cm^{-1} for the mono and broad water band at ~3480 cm^{-1} for the bis. The bis-complex electronic absorption spectrum also shows a broad ligand field band at 15.6 kK in addition to the ~21.6 kK charge transfer band, whereas the mono-complex possesses only the ~21.6 kK band. This difference suggests that the bis-complex is hexacoordinated, whereas the mono-complex has a tetracoordinated square planar configuration. Further evidence is provided by the X-ray photoelectron spectra; the binding energies of the silver $3d_{3/2,5/2}$ levels move to lower energies in the bis-complex.

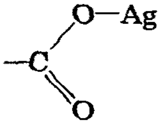
$Ag(terpy)S_2O_8 \cdot H_2O$	$3d_{3/2}$	374.5 eV	$3d_{5/2}$	368.4 eV
$Ag(terpy)_2S_2O_8 \cdot 3\,H_2O$		373.4		367.2

A hexacoordinated $Ag(N_6)$ type would have negative charge build-up at the metal center, resulting in a decrease in metal core binding energies compared to the tetracoordinated $Ag(N_3O)$ type.

(ii) Pyridine monocarboxylic acid complexes of Ag(II)

$Ag(pic)_2$, $Ag(nic)_2$ and $Ag(isonic)_2 \cdot H_2O$

The positions of the carboxylate groups in the pyridine rings for picolinate, nicotinate and isonicotinate ions are 2-, 3-, and 4-, respectively. These neutral complexes have been prepared by the method of persulfate oxidation [2,36—38]. Bis(picolinato)silver(II) is orange-red, whereas bis(nicotinato)silver(II) and bis(isonicotinato)silver(II) are cinnamon-red or orange-brown powders. Infrared absorption spectra of these complexes show the ~1700 cm^{-1} asymmetric carbonyl stretch of the free —COOH group shifted to ~1630 cm^{-1} in the complexes characterizing the silver—carboxylate bonding of the following structure [38,39]. These compounds are of neutral



charge and are insoluble in most solvents, suggesting that the $—COO^-$ group serves both to neutralize the charge on the silver ion and to fill in the coordination space. Far-IR spectra have also confirmed the presence of silver—nitrogen bonds [40].

The X-ray powder patterns have been obtained with all three compounds [38,41,42], but the structures cannot be completely elucidated based on these patterns. Single crystals could not be prepared by these authors.
A square planar configuration for $Ag(pic)_2$ has been assigned based on the isomorphism of Ag(II) and Cu(II) bis(picolinato) complexes [42]. Additional

support comes from the diffuse reflectance spectra of these complexes. All have absorption maxima at values ~25 kK and higher in agreement with other known square planar Ag(II) complexes [36] (Table 3). The structure of $Ag(pic)_2$ is shown in Fig. 2. X-ray powder data on $Ag(nic)_2$ and $Ag(isonic)_2$ lead to several proposed polymeric structures for these square planar complexes and none appear to be very conclusive [36,38,41].

Magnetic moment measurements as a function of temperature show that with the exception of $Ag(nic)_2$, the compounds obey Curie—Weiss behavior from 83 to 309 K with a Weiss constant $\theta \leqslant 10$ K. Only $Ag(nic)_2$ shows evidence of antiferromagnetic interaction with $\theta = 52$ K [38]. Eckberg and Hatfield [43], however, reported a θ of 42 K. Since only one compound $[Ag(py)_4]S_2O_8$ has been known to follow Curie law down to 1.6 K [8], the magnetic susceptibility of $Ag(nic)_2$ was reinvestigated as a function of temperature from 275 K to 4.2 K [44]. The low temperature—susceptibility data shows a maximum of susceptibility at 40 K. This behavior is evidence of an exchange interaction in a silver(II) complex. Several models were used to fit the susceptibility—temperature data, such as the Bleany—Bowers' dimer model, isotropic Heisenberg model and the Ising model. However, only the anisotropic Ising model of the simplest polymeric system of a one-dimensional chain-type structure fits the data. The Hamiltonian describing magnetic interaction along a chain of metal ions is

$$H = -J \sum_{i=1}^{N} [S_{iz} \cdot S_{(i+1)z} + \gamma(S_{ix} \cdot S_{(i+1)x} + S_{iy} \cdot S_{(i+1)y})]$$

where $J = -30.8 \pm 1.0$ cm^{-1} is the exchange energy, $S = 1/2$ and γ varies from 0 to 1. This result is of interest, since few chains (none of silver(II)) are known to show Ising behavior. The structure of $Ag(nic)_2$ in the Ising model suggests that a chain-like pathway magnetic interaction between silver(II) must be allowed for.

The g-tensor values showing anisotropy (from EPR) are listed in Table 2.

(iii) Pyridine dicarboxylic acid complexes of Ag(II)

$Ag(quinH)_2 \cdot 2H_2O$, $Ag(isocinchH)_2$, $Ag(cinchH)_2 \cdot 2H_2O$, $Ag(lutH)_2$ and $Ag(dipic)(dipicH_2) \cdot xH_2O$ ($x = 4$ or 1)

Silver(II) forms complexes with pyridine-dicarboxylic acids such as

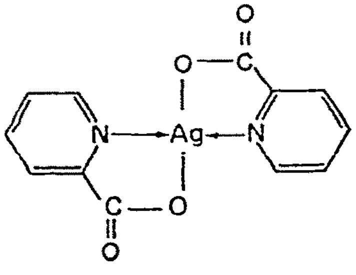


Fig. 2. Bis(pyridine-2-carboxylato)silver(II).

TABLE 3

Electronic absorption maxima of Ag(II) and Ag(III) complex compounds

Ag compound	Absorption max. (kK)(ϵ, l mol^{-1} cm^{-1})	Ref.
$[Ag(py)_4]S_2O_8$	~22 [a]	13
	20.4 [b]	14
$Ag(3\text{-}Mepy)_4(S_2O_8)$	26.3	15
$Ag(4\text{-}Mepy)_4(S_2O_8)$	27.0	15
$[Ag(bipy)_2]X_2$	22 (1600) [c]	14
	34.1, 22 (1900) [c]	25
	22 (2160 ± 40) [c]	24
$[Ag(phen)_2]S_2O_8$	31.0_6(sh), 32.6_8(sh) [c]	62
$Ag(pic)_2$	44.2, 38.4, 30.0, ~24.5(s) [a]	38
$Ag(nic)_2$	44.6, 38.2, 33.0, ~25.0, ~21.0(s) [a]	38
$Ag(isonic)_2 \cdot H_2O$	44.8, 37.4, 35-24 vbr (s) [a]	38
$Ag(quinH)_2 \cdot 2\ H_2O$	45.1, 37.3, ~30.2 vbr, 22.8 [a]	38
	18.0 [b]	14
$Ag(isocinchH)_2$	45.0, 36.2, ~29.3 br	38
$Ag(dipic)(dipicH_2) \cdot 4\ H_2O$	44.8, 37.0, ~30 vbr, ~24.0 br, 15.6 [a]	38
	37.0, 29.0 br, 25.5 br, 16.7	48
	17.4 (800), 11.0 (500) [c]	48
$Ag(cinchH)_2 \cdot H_2O$	44.5, ~36.8 s, ~31.2 br, ~23.4 br(s) [a]	38
$Ag(pyz)_2S_2O_8$	37.4, 32.7, 25.8, 19.0 [a]	52
$Ag(pyzCOO)_2$	37.4, 29.6, 20.6 [a]	52
$Ag(dipic)(terpy) \cdot 4\ H_2O$	14.4 [a]	50
	15.2 (240—250) [c]	51
$Ag(dipic)(terpy)(S_2O_8)_{0.5}$	15.2 (240—250) [c]	51
$Ag(dipic)(terpy)(ClO_4) \cdot 2\ H_2O$	15.2 (240—250) [c]	51
$Ag(dipic)(bipy) \cdot 3\ H_2O$	13.1 vbr [c]	51
$Ag(terpy)S_2O_8 \cdot H_2O$	21.6 [c]	35
$Ag(terpy)_2S_2O_8 \cdot 3\ H_2O$	21.6 (1380), 15.6 [c]	35
AgOEP	24.4 (219,000), 19.0 (12,500), 17.9 (18,000) [d]	72
AgTPP	22.3_2 (19,500), 18.5_2 (17,000), 17.3_6 [e]	74,75
$Na_4[AgTPPS]$	18.5 [f]	62
Ag(PPDE)	23.9_2 (246,800), 18.7 (15,800), 17.5 (24,100) [e]	67
	23.9_5 18.7_3 17.5_4 [g] CCl_4	67
Ag(MPDE)	19.0, 17.89 [h]	66
	19.1_2 (14080), 17.99 (19,590) [i]	67
Ag(phthalocyanine)	28.73, 16.37, 15.41, 14.77 [j]	26
(Ia)	35.71 (3600), 28.74 (7,700) [k]	4
(IIa)	36.36 sh(3000), 29.24 (13300) [k]	4
(III)	33.33 (2000), 26.2 (8600) [k]	4
(IV)	33.33 (6200), 2959 (6200) [k]	4
$Ag(III)OEP(ClO_4)$	24.75 (131,000), 19.38 (9800), 18.11 (25,200) [d]	72
$Ag(III)TPPS^{3-}$	19.2 [f]	62

[a] Diffuse reflectance; [b] crystal; [c] aqueous solution; [d] $CHCl_3$/methanol; [e] benzene; [f] methanol; [g] CCl_4; [h] $CHCl_3$; [i] dioxane; [j] 1-chloronaphthalene; [k] 10^{-3} M complex, 10^{-1} M $(C_2H_5)_4NClO_4$ in CH_3CN.

quinolinic (2,3-), isocinchomeronic (2,5-), dipicolinic (2,6-), cinchomeronic (3,4-), and lutidinic (2,4-) acids [2,38,44—49]. These compounds are dark red in color and sparingly soluble in water. Earlier, X-ray diffraction studies on polycrystalline samples of these compounds did not lead to the interpretation of the structures, although it was suggested that the cinchomeronic acid—silver(II) complex could be related to $Ag(nic)_2$, due to the dicarboxyl groups location at 3,4-positions [2,41]. The magnetic susceptibility values at room temperature for the mono- and dicarboxylic acid complexes are slightly lower than usual (Table 1). Curie—Weiss behavior with $\theta \leqslant 10$ K is obeyed except for $Ag(dipic)(dipicH_2) \cdot 4\ H_2O$, which has $\theta = 0°$. This is thought to arise from a structural difference in the latter complex, a fact supported by the electronic absorption maximum at $\sim$17 kK. Infrared data shows the presence of free —COOH groups and coordinated COO^- groups in the complexes. In addition, there exists a weak ν(O—H) band corresponding to hydrogen bonding in carboxylic acid groups. Water molecules in hydration are apparently involved in H-bonding. With the exception of $Ag(dipic)(dipicH_2) \cdot 4\ H_2O$, the other pyridine dicarboxylate complexes appear to have square planar structures as indicated by their electronic absorption spectra above $\sim$21 kK (Table 3). Although the dihydrate of the dipicolinate complex has been reported, only the mono- and tetrahydrate were obtained in a recent study [48].

Recently an X-ray crystal diffraction study of the pyridine 2,6-dicarboxylic acid complex, $Ag(dipic)(dipicH_2) \cdot H_2O$ has revealed a hexacoordinated complex with a very highly distorted octahedral structure [47,48] (Fig. 3). The two ligands coordinated to the silver atom are different. One can be described as dianionic (dipic) and the other a neutral ligand $dipicH_2$. With the dianionic ligand, Ag forms strong single bonds to N (2.09 Å) and to the two negatively charged O atoms (2.20 Å), but with the neutral ligand, Ag is bonded less strongly to N (2.20 Å) and the two ketonic O atoms (2.54 Å). The O—Ag—N bond angles in the dianionic-Ag unit (right in Fig. 3) and neutral ligand-Ag (left in Fig. 3) are respectively 76.6° and 71.6°, indicative of the very highly distorted octahedral structure. The two ligands are approximately planar and intersect at 83.4°. The complex molecule can be assigned C_2 symmetry.

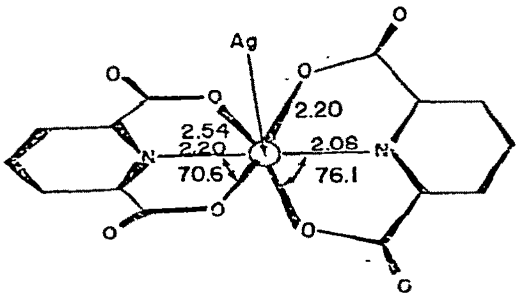


Fig. 3. Distorted octahedral structure of hexacoordinated $Ag(dipic)(dipicH_2) \cdot H_2O$.

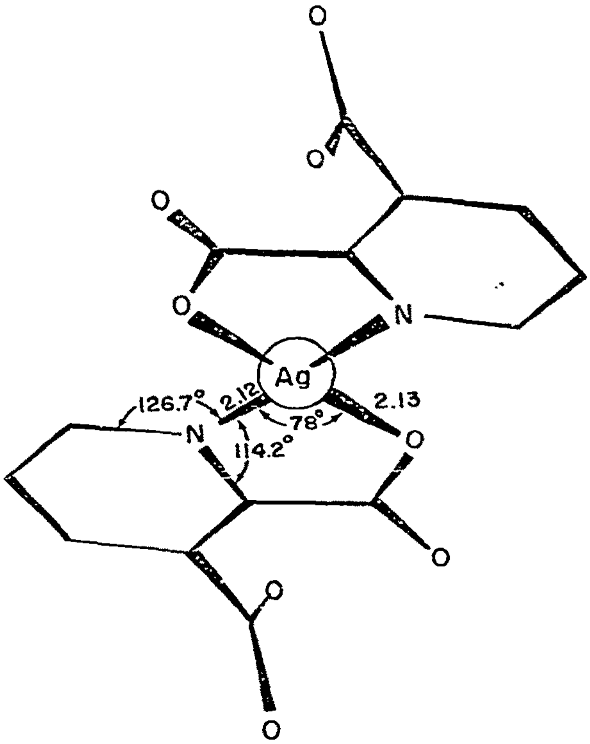


Fig. 4. Structure of $Ag(quinH)_2 \cdot 2\,H_2O$.

The structure of the silver(II)—pyridine 2,3-dicarboxylic complex, $Ag(quinH)_2 \cdot 2\,H_2O$ is shown in Fig. 4. The silver atom is strongly bonded to a N atom (2.12 Å) and to an O atom (2.13 Å) of the $—COO^-$ at the 2-position. The pyridine rings are planar, but the five-membered rings formed by the chelation of Ag by pyridine N and 2-carboxylate oxygen are non-planar with an O—Ag—N bond angle of 78.0°. The structure is a tetragonally

TABLE 4

Structural information of Ag(II) complexes

Parameters	Compound		
	$Ag(bipy)_2S_2O_8$	$Ag(quinH)_2 \cdot 2\,H_2O$	$Ag(dipic)(dipicH_2) \cdot H_2O$
Ag—N (Å)	2.14—2.18	2.12	2.09
Ag—O (Å)		2.13	2.20
Bond angle	77° (N—Ag—N)	78° (N—Ag—O)	76.6° (N—Ag—O, dipic) 71.6° (N—Ag—O, $dipicH_2$)
Complex configuration	Square planar approximate	Square planar approximate	Distorted octahedral

distorted octahedron, if one takes into consideration the weak interaction (2.97 Å) between the silver atom and the ketonic oxygens at the 3-position of two adjacent molecules stacked in axial direction.

The X-ray crystal diffraction data provide important bond length information on Ag(II) complexes, listed in Table 4.

(iv) Mixed ligand complexes of Ag(II) [50,51]

The crystal structure determination of Ag(dipic)(dipicH$_2$) · H_2O shows unambiguously a hexacoordinated complex. The tridentate dipicH$_2$ ligand being weakly coordinated to the silver ion can be expected to be replaced by other ligands in substitution reactions. When it is allowed to react in aqueous solution with bipy, phen, or terpy, mixed ligand complexes of the general formula Ag(dipic)(L) · $x H_2O$ are produced. Other complexes of the type Ag(pyridine-carboxylato)(S_2O_8)$_{1/2}$ · $x H_2O$ are also synthesized by mixing Ag(II)(pyridine-carboxylato) complexes, terpy and an excess of $(NH_4)_2S_2O_8$. All told, nine compounds of silver(II) with mixed ligands are prepared. They are listed in Table 1 (those with ref. 51). Magnetic moments obtained on these new series of compounds confirm the silver(II) oxidation state. X-ray powder data and IR spectra measurements from 4000—600 cm^{-1} on Ag(pic)(terpy)(S_2O_8)$_{1/2}$ · 2 H_2O when compared with data from [AgL_2]X_2 (L = pic, terpy, or lutH) confirm discrete mixed ligand existence.

The IR spectra of Ag(dipic)(L) · $x H_2O$ show the definite disappearance of the dipicH$_2$ (νCOOH) absorption bands in the region 1750—1700 cm^{-1}. The strong ν_{asym}COO$^-$ bands remain near 1650—1600 cm^{-1}, suggesting RCOO—Ag bonding.

Similar electronic spectra with maximum at ~15.2 kK (ϵ 240—250), have been obtained when Ag(dipic)(terpy) · 4 H_2O, Ag(dipicH)(terpy)(S_2O_8)$_{1/2}$ · 2 H_2O and Ag(dipicH)(terpy)(ClO_4) · 2 H_2O are placed in aqueous solution. Apparently, a common species in water is produced. The diffuse reflectance measurements on several of these mixed ligand complexes of silver(II) (Table 3) indicate higher coordination numbers of 5 or 6, rather than square planar geometry. These compounds all show limited solubility in water to form brown solutions. Remarkably, the species in aqueous solution are rather stable toward reduction to silver(I). This enhanced solubility and stability have also been reported in the case of Ag(terpy)$_2S_2O_8$ · 3 H_2O [35]. This could be attributed to the strong complexing influence of terpy and the increase in coordination number. The hexacoordinated species are found to be the most soluble and stable in aqueous solution.

(v) Pyrazine and pyrazine carboxylic acid complexes of Ag(II) [52]

The conventional method of persulfate oxidation has been employed to prepare three new silver(II) pyrazine and pyrazine carboxylic acid complexes. Elemental analysis and magnetic studies confirm the silver(II) ions and the

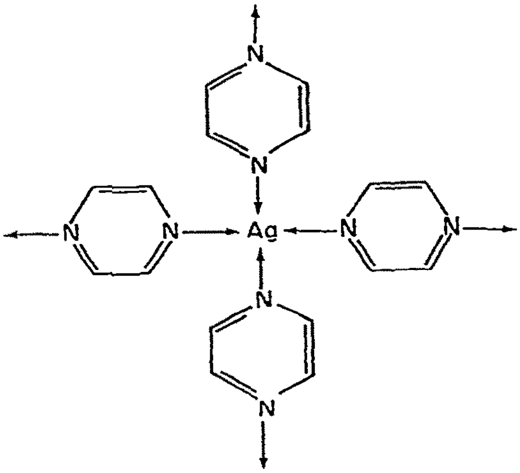


Fig. 5. Square planar structure of [$Ag(pyz)_2$]S_2O_8.

following formulae for the compounds

$Ag(pyz)_2S_2O_8$, $Ag(pyz\text{-}2\text{-}COO)_2$ and $Ag_2(I)Ag(II)(pyz\text{-}2,3\text{-}(COO)_2)_2$

The diffuse reflectance spectrum of $Ag(pyz)_2S_2O_8$ shows *d—d* transition at 19 kK (Table 3) consistent with a square planar configuration. This might be expected by analogy with the pyridine complex $Ag(py)_4S_2O_8$. However, the appearance of weak pyrazine bands in the 950—1000 cm^{-1} region indicates bridging pyrazine molecules arising from polymeric chain (Fig. 5). This is further supported by antiferromagnetic behavior from the magnetic susceptibility versus temperature (83—299 K) dependence data revealing a Curie—Weiss constant of 84 K. An analogous situation occurs with $Ag(nic)_2$ whose structure is believed to be polymeric. Magnetic interactions across pyrazine and quinoxaline bridges have been established in compounds $Cu(pyz)(NO_3)_2$ and $Cu(quinox)(NO_3)_2$ [53,54].

The bis(pyrazine-2-carboxylato)silver(II) complex has intense IR absorption at 1620 and 1334 cm^{-1} characteristic of a —COO—Ag bond. The magnetic behavior is normal with $\theta = 8$ K and a square planar structure for the magnetically dilute species is proposed based on the electronic absorption at 20.6 kK. The structure would be analogous to $Ag(pic)_2$.

The X-ray powder pattern of $Ag_2(I)Ag(II)(pyz\text{-}2,3\text{-}(COO)_2)_2$, a mixed silver(I) and silver(II) complex of pyrazine-2,3-dicarboxylate, shows the existence of a discrete silver(I) and silver(II) complex, rather than a mixture. Infrared examination leads to the proposed structure shown in Fig. 6. Recent EPR, PMR, and IR studies of the complex by Berenblym et al. [55] have supported the proposed structure in which the spin density is being transferred from the paramagnetic silver nuclei to the pyrazine ring. The prepara-

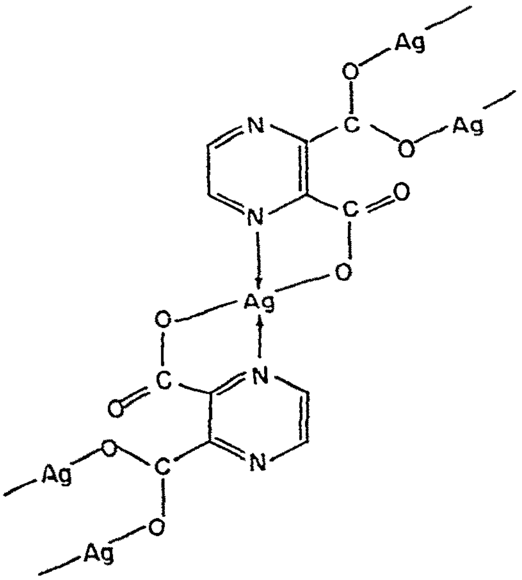


Fig. 6. Proposed polymeric structure of $Ag_2(I)Ag(II)(pyz\text{-}2,3\text{-}(COO)_2)_2$.

tion of a pyrazine-2,3,5-tricarboxylic acid silver(II) complex failed to give a stoichiometric product.

(vi) Other complexes of Ag(II)

Complexation with pyridine tricarboxylic acids (2,3,6-, 2,4,5-, and 2,4,6-) has been reported [56]. They have magnetic moments of 1.73—1.82 BM, and appear to be the least stable among the complexes of pyridine carboxylic acids. Oxine (8-hydroxyquinoline) does not form complexes with silver(II) [57]. The earlier reported $Ag(oxine)_2$ is erroneous [58].

Bidentate anion ligands containing sulfur atoms, such as *N*,*N*-dialkyl-dithiocarbamates, can stabilize divalent cations such as Cu and Ag [59,60]. The stable $Ag[(iso\text{-}C_3H_7)_2NCS_2]_2$ has been prepared and EPR data show isotropic anisotropy with *g*-values listed in Table 2. The apparent structure is shown in Fig. 7.

Recently, bis(isoquinoline-1-carboxylato) silver(II) has been prepared from hot solution (75°) as an orange precipitate. The physical data for this complex are listed in Tables 1 and 5.

C. KINETIC STUDIES ON SILVER(II) COMPLEXES

The kinetics on the oxidation of $Ag(bipy)^+$ by $S_2O_8^{2-}$ have been studied in 50% acetone solution [61]. The observed rate law is

$$\text{Rate} = k[S_2O_8^{2-}][Ag(bipy)_2^+] \tag{4}$$

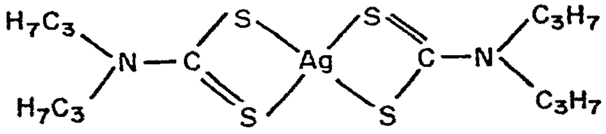


Fig. 7. Square planar structure of bis(isopropyldithiocarbamate)silver(II).

The stoichiometry determined is $[\mathrm{Ag(bipy)}_2^+] : (\mathrm{S_2O_8^{2-}}) = 2 : 1$. The Arrhenius activation energy obtained is 9.5 ± 1.0 kcal mole^{-1} and the value of $\log_{10}A$ is 7.6. A one-electron exchange mechanism has been postulated with $\mathrm{SO_4^-}$, further oxidizing the $\mathrm{Ag(bipy)_2^+}$.

The poor solubility of silver(II) complexes and their instability in aqueous solution limits kinetic studies where they could be employed as square planar one-electron oxidants. The slow rate of decomposition of $\mathrm{Ag(bipy)_2^{2+}}$ and $\mathrm{Ag(phen)_2^{2+}}$ in aqueous solution have been reported earlier [25] with possible three parallel paths. However, we have re-examined the kinetics of $\mathrm{Ag(bipy)_2^{2+}}$ in aqueous solution [62] and it appears to be more complicated with sigmoidal pH—kinetic behavior and second-order dependence in $[\mathrm{Ag(bipy)_2^{2+}}]$. The hydrogen peroxide reduction of $\mathrm{Ag(bipy)_2^{2+}}$ has been studied in the stopped-flow apparatus [24]. The sigmoidal pH—kinetic dependence is explained by a mechanism involving $\mathrm{Ag(Hbipy)_2^{4+}}$. The derived rate law conforms to the observed rate law,

$$-\mathrm{d}\ln[\mathrm{Ag(bipy)_2^{2+}}]/\mathrm{d}t = \frac{2a(1 + b[\mathrm{H^+}]^2)}{(1 + c[\mathrm{H^+}]^2)}[\mathrm{H_2O_2}] \tag{5}$$

The activation parameters obtained are $\Delta H = 11.9$ kcal mole^{-1} and $\Delta S = 3.1$ eu with $k(25°) = 1.30 \times 10^3$ M^{-1} s^{-1} at a pH of 5.7.

In 0.5 M $\mathrm{H_2SO_4}$, $\mathrm{Ag(phen)_2^{2+}}$ and $\mathrm{Ag(bipy)_2^{2+}}$ oxidize $\mathrm{Fe^{2+}}$ following the second-order rate law, the k values at 25.0° are 1.7×10^6 and 1.4×10^6 M^{-1} s^{-1}, respectively [63].

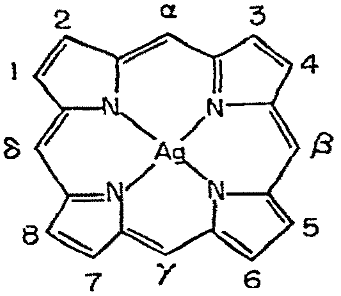
Seebach [64] has carried out a series of silver(II) reactions with various quinoline derivatives at 0—5°. Several silver(II)—quinoline intermediates have been observed with absorption bands at 16.5 kK. The quinolines that form intermediates with Ag(II) are 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulfonate, 5-chloro-8-hydroxy-quinoline, and 5,7-dichloro-8-hydroxyquinoline.

Exchange reactions of the $\mathrm{Ag^{110}}$ ion between $\mathrm{AgNO_3}$ and $\mathrm{Ag(bipy)_2^{2+}}$ and $\mathrm{Ag(phen)_2^{2+}}$ compounds show that total exchange occurred after two minutes [65].

D. MACROCYCLIC AMINE COMPLEXES OF SILVER(II) AND SILVER(III)

(i) Porphinato complexes of Ag(II) and Ag(III)

Several porphyrin complexes of Ag(II) and Ag(III) have been prepared [3]. These are the mesoporphyrin IX dimethyl ester [66], protoporphyrin IX



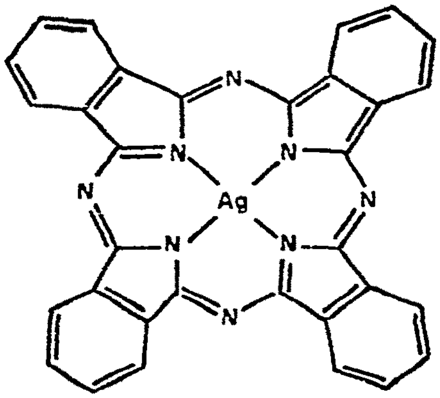


Fig. 8. Porphinato complex of silver(II) and silver(III).
Abbreviation = substituted porphyrin. TPP = $\alpha, \beta, \gamma, \delta$-tetraphenyl-porphyrin; TPPS = α, β, γ, δ-tetra-(*p*-sulfonatophenyl)-porphyrin; DPDE = deuteroporphyrin IX dimethyl ester; EPDE = etioporphyrin II dimethyl ester; PPDE = protoporphyrin IX dimethyl ester; MPDE = mesoporphyrin IX dimethyl ester; OEP = octaethylporphyrin.
Substituents on porphyrin ring

	1	2	3	4	5	6	7	8
DPDE	M	H	M	H	M	P	P	M
PPDE	M	V	M	V	M	P	P	M
MPDE	M	E	M	E	M	P	P	M
EPDE	M	E	E	M	M	E	E	M
OEP	M	M	M	M	M	M	M	M

M = CH_3; E = CH_2CH_3; P = $CH_2CH_2COOCH_3$; V = $CH{=}CH_2$.

Fig. 9. Phthalocyanine—silver(II) complex.

dimethyl ester [67], deuteroporphyrin IX dimethyl ester [68], etioporphyrin II dimethyl ester [69], octaethylporphyrin [70—73], tetraphenylporphyrin [74,75], tetra(*p*-sulfonatophenyl) porphyrin [62], and phthalocyanine [26] (Figs. 8 and 9). The method of preparation generally followed the disproportionation reaction described in Sect. B. Magnetic measurements show that the paramagnetic silver(II) is in the cavity of the porphyrins [26,68]. EPR studies on the deuteroporphyrin IX dimethyl ester, and phthalocyanine complexes of silver(II) species show isotropic g values consistent with the planar structure. In one case, the first derivative in the EPR spectrum shows a symmetric hyperfine pattern consisting of eleven lines, explained by the overlap of two sets of nine nitrogen hyperfine lines. The odd electron can be found for the two systems to be in the $d_{x^2-y^2}$ orbital about 58% and 54% of the time for Ag(DPDE) and Ag(phthalocyanine) respectively. These values suggest the much greater covalent character in the B_{1g} molecular orbital for the silver complexes than the copper complexes.

The typical electronic absorption spectra of silver(II) and silver(III) porphyrins are characterized by a two-banded visible absorption pattern (500—

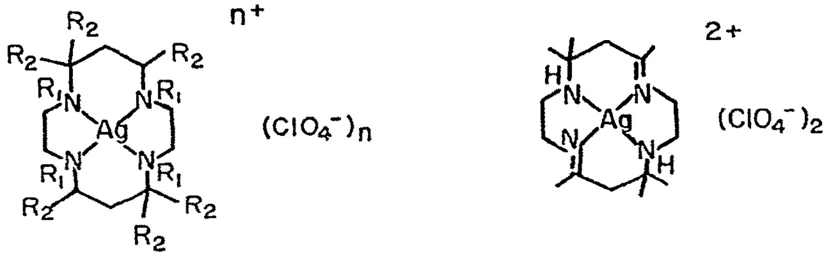
600 nm) and an intense Soret band below 450 nm [66,67,72].

Ag(II) OEP and Ag(II) TTPS are easily oxidized to the corresponding Ag(III) complexes by chemical or electrochemical means. Cyclic voltammetry with AgOEP has shown that the oxidation step occurred at the central metal, and not at the porphyrin ring. The measured Ag(III)OEP/Ag(II)OEP couple is 0.44 V [71,72]. The EPR and X-ray photoelectron studies on Ag(II)OEP and Ag(III)OEP (ClO_4) have shown that both are planar and further establish that Ag(III)L is formed by removing an electron [73] from the Ag(II) and not the porphyrin ring as in the cases of Zn^{2+} and Mg^{2+} OEP complexes.

(ii) Tetraaza complexes of Ag(II) and Ag(III)

The perchlorate salt of several tetraaza complexes of silver(II) ((Ia), (IIa), (III) and (IV) in Fig. 10) have been prepared by the disporportionation method [4]. The colors of the salts vary from yellow to dark orange-brown. (Ia) and (IIa) can be oxidized to the corresponding Ag(III) complexes, (Ib) and (IIb) with $NOClO_4 \cdot H_2O$ in acetonitrile. The +3 complexes are soluble in water forming violet solutions which eventually fade to yellow color. EPR studies indicate formation of Ag(II)-L. A probable mechanism analogous to the decomposition of the corresponding Ni(III)-tetraaza complexes has been postulated.

The tetraaza complexes are stable in many solvents (acetonitrile, water, and ethanol) in which they are soluble. EPR studies show axial systems typical of planar complexes for (Ia) and (IIa). In the case of (III), $g_{\parallel} < g_{\perp}$ which could be due to strong interaction with ClO_4^- in the solid state.



Ia : $R_1 = H$, $R_2 = CH_3$; n=2

b : n = 3

IIa : $R_1 = H$; $R_2 = H$; n=2

b : n = 3

III : $R = CH_3$; $R_2 = H$; n=2

IV

Fig. 10. Tetraaza complexes of silver(II) and silver(III) perchlorate.

In nitric acid, (Ia) and (IIa) form orange solutions which are diamagnetic, suggesting that nitric acid also oxidizes the silver(II) to the 3+ state. It appears that these strong tetraaza ligands raise the antibonding *d* orbitals in the low oxidation state species to such a high level that electrons are easily removed.

E. AMINE COMPLEXES OF SILVER(III)

Biguanides, substituted biguanides [76], ethylenebis(biguanide) [77—79], and piperazine dibiguanide [80] have been found to complex and stabilize silver(III). Less certain has been the report of the preparation of a Ag(III)-oxine compound [81]. Persulfate oxidation of silver nitrate in the presence of these ligands for the first three cases required pH $\geq$ 6.5 solution. The colors of the silver(III) complexes vary from red to dark brown. From oxidimetric titrations, conductometric measurements and the diamagnetic ($4d^8$) nature of the compounds the oxidation state of the silver ion is definitely three. Apparently, the silver(II) complexes of these ligands cannot be prepared [2].

The piperazine dibiguanide silver(III) compounds prepared are [Ag(III)-pipz(bigH)$_2$]X$_3$ where X = OH$^-$, NO$_3^-$, or 3/2 SO$_4^{2-}$ · 1/2 H$_2$O [80]. These compounds are sparingly soluble in water but insoluble in alcohol, chloroform, acetone, ether, DMF and diacetone alcohol. The biguanide and substituted biguanide—silver(II) complexes prepared have the general formula [Ag(bigH)$_2$]X$_3$ and [Ag(mebigH)$_2$]X$_3$ where X = NO$_3^-$, OH$^-$, 3/2 SO$_4^{2-}$ or mixed anions [76]. Generally, some water of hydration is incorporated in the compounds.

The ethylenebis(biguanide) complex of silver(III) of composition Ag(enbisbig)X$_3$ where X = HSO$_4^-$, NO$_3^-$, OH$^-$, ClO$_4^-$, or mixed anions were the first to be prepared [2, 77—79]. Recent X-ray crystal structures [82] and photo-

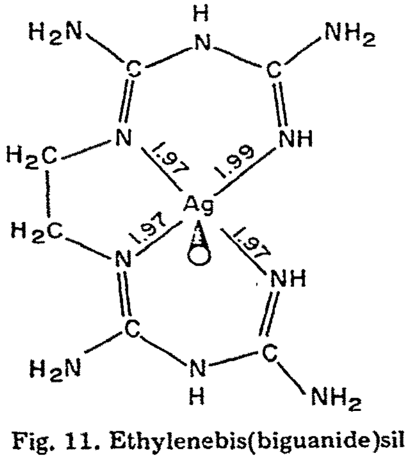


Fig. 11. Ethylenebis(biguanide)silver(III) perchlorate.

electron spectroscopy [83] studies on the perchlorate crystal by Zatko and Prather have revealed that the silver atom lies in a plane coordinated strongly to four N atoms (Ag(III)—N = 1.97—1.99 Å. This is ~0.18 Å less than Ag(II)—N) and weakly bonded to a perchlorate oxygen at 2.82 Å above the plane, (Fig. 11). The biguanide units are essentially planar and the enbisbig framework is bowed away from the ClO_4^-. Photo-electron spectra further establish that little charge delocalization takes place from the silver to the ligand. This leaves the silver with a high positive charge. A similar situation is observed in the case of $Na_5H_2Ag(IO_6)_2$ [84].

Complicated decomposition kinetics of ethylenebis(biguanide)silver(III) nitrate in water has been reported [85]. The complex solution has a wide band from 300—370 nm (ϵ 2325—2522) at 32°. A pK of 54.16 (32°) has been reported for the instability constant of reaction (6) [86].

$$\mathrm{Ag(III)(enbisbig)^{3+} = Ag^{3+} + enbisbig} \qquad (6)$$

Reinvestigation of the hydrolysis of ethylenebis(biguanide)silver(III) in aqueous solution shows the oxidation of water to hydrogen peroxide or hydroxyl radical [87]. The kinetics in various pH solutions and temperatures (25—40° C) yield first-order in complex concentration, inverse H^+ effect, and Ag^+ catalysis. At constant pH, the observed rate law is

$$-\mathrm{d(complex)}/\mathrm{d}t = (k_A + k_B[\mathrm{Ag^+}])[\mathrm{complex}] \qquad (7)$$

E_a values of 3.7 and 15.2 kcal mole^{-1} have been reported for the hydrolysis of the complexes, $[\mathrm{Ag(enbisbig)}](\mathrm{NO_3})_3$ and $[\mathrm{Ag(enbisbig)(HSO_4)}](\mathrm{NO_3})_2$, respectively.

The kinetics of the oxidation of $\mathrm{Ag(enbisbig)^+}$ to Ag(III) by $S_2O_8^{2-}$ consits of two consecutive pseudo-first-order reactions in $\mathrm{Ag(enbisbig)^+}$ at excess $[S_2O_8^{2-}]$ [61]. The orders of reaction in $[S_2O_8^{2-}]$ for the two reactants are both 1.0. The activation energies for the two consecutive reactions (8) and (9) are 13.1 ± 0.7 and 14.3 ± 3.8 kcal mole^{-1} ; the corresponding values for $\log_{10}A$ are 7.7 and 9.6, respectively. The mechanism which conforms to the rate law is

$$\mathrm{Ag(enbisbig)^+ + S_2O_8^{2-} \rightarrow Ag(enbisbig)^{2+} + X} \qquad (8)$$
$$\mathrm{Ag(enbisbig)^{2+} + S_2O_8^{2-} \rightarrow Ag(enbisbig)^{3+} + X} \qquad (9)$$

where X may be $S_2O_8^{3-}$ or both SO_4^- and SO_4^{2-}. X does not react with $\mathrm{Ag(enbisbig)^+}$, but could probably oxidize H_2O.

F. X-RAY PHOTO-ELECTRON SPECTROSCOPY STUDIES ON SILVER(II) AND SILVER(III) COMPLEX COMPOUNDS

Recently, X-ray photo-electron spectroscopy [35,50,73,83] has been used to show the following trends: (a) an increase in the core electron binding energies of metal core electrons with increase in metal oxidation state; (b) a dependence of binding energies on ligand electronegativity and π-accep-

TABLE 5

X-ray photo-electron information on 3*d* binding energies of Ag(0), Ag(I), Ag(II), and Ag(III) complex compounds

Compound	$3d_{3/2}$ (eV)	$3d_{5/2}$ (eV)	Ref.
Silver(0)			
Ag deposited on Pt foil	372.4	366.8	83
Ag(0) evaporated on gold foil	374.0	367.9	73
Silver(I) complexes			
Ag_2O	374.1	368.6	83
Ag_2SO_4	374.0	368.6	83
AgBr	373.8	368.2	83
$Ag(terpy)NO_3 \cdot 2\,H_2O$	374.0	368.0	35
$Ag(bipy)_2NO_3 \cdot 2\,H_2O$	374.1	368.1	50
$Ag(phen)_2NO_3 \cdot H_2O$	374.1	368.1	50
"Ag(pic)", low pH form	374.1	368.1	50
"Ag(pic)", high pH form	374.4	368.2	50
$Ag_2(dipic) \cdot H_2O$	374.5	368.5	50
$Ag(pyzCOO)_2$	374.1	368.0	50
$Ag_2(pyz\text{-}2,3\text{-}(COO)_2)$	374.1	368.2	50
$Ag_3(pyz\text{-}2,3,5\text{-}(COO)_3) \cdot H_2O$	374.2	368.2	50
Silver(I)—silver(II) complexes			
$Ag(I)_2Ag(II)(pyz\text{-}2,3\text{-}(COO)_2)_2$	374.1	368.1	50
Silver(II) complexes			
$Ag(phen)_2(NO_3)_2$	373.9	368.2	83
$Ag(bipy)_2S_2O_8 \cdot H_2O$	373.9	368.0	50
$Ag(bipy)_2(NO_3)_2 \cdot H_2O$	374.0	368.5	83
$Ag(pic)_2$	374.2	368.0	50
$Ag(isonic)_2 \cdot H_2O$	373.9	367.9	50
$Ag(isoquin\text{-}1\text{-}COO)_2$	374.1	368.0	50
$Ag(quinH)_2 \cdot 2\,H_2O$	373.6	367.6	50
$Ag(isocinchH)_2$	375.1	369.0	50
$Ag(lutH)_2 \cdot 2\,H_2O$	374.1	368.2	50
$Ag(cinchH)_2 \cdot H_2O$	374.5	368.5	50
$Ag(dipic)(dipicH_2) \cdot 4\,H_2O$	372.9	366.9	50
$Ag(dipic)(dipy) \cdot 3\,H_2O$	373.6	367.7	50
$Ag(dipic)(phen) \cdot 7/2\,H_2O$	373.7	367.6	50
$Ag(dipic)(terpy) \cdot 4\,H_2O$	373.6	367.6	50
$[Ag(dipicH)(terpy)](S_2O_8)_{0.5} \cdot 2\,H_2O$	373.8	367.7	50
$[Ag(quinH)(terpy)](S_2O_8)_{0.5}$	373.9	367.7	50
$[Ag(lutH)(terpy)](S_2O_8)_{0.5} \cdot H_2O$	373.8	367.8	50
$[Ag(isocinhH)(terpy)](S_2O_8)_{0.5}$	374.0	368.1	50
$[Ag(pic)(terpy)](S_2O_8)_{0.5} \cdot 2\,H_2O$	373.7	367.7	50
$Ag(terpy)S_2O_8 \cdot H_2O$	374.5	368.4	35
$[Ag(terpy)_2]S_2O_8 \cdot 3\,H_2O$	373.4	367.2	35
AgOEP	374.3	368.3	73
AgTPP	373.7	367.6	73
Silver(III) complexes			
$[Ag(enbisbig)]_2(S_2O_8)_3$	377.3	371.4	83
$Na_5H_2Ag(IO_6) \cdot 16\,H_2O$	377.0	371.0	83
$AgOEP(ClO_4)$	377.1	371.0	73

tor ability. Another possible useful trend in silver(II) complexes is a decrease in binding energies for complexes with apparently higher coordination numbers.

The $3d_{3/2}$ and $3d_{5/2}$ binding energies for Ag(0), Ag(I), Ag(II), and Ag(III) are listed in Table 5. Carbon 1*s* binding energy at 284.0 eV is used as reference for all cases. The silver(I) complexes exhibit narrower and more symmetric peaks with relatively low half-widths (FWHM = 1.1 ± 0.1 eV) than the Ag(II) and Ag(III) complexes. The average FWHM values for Ag(II) is 2.4 ± 0.5 eV. However, in Ag(dipic)(dipicH$_2$) · 4 H$_2$O and [Ag(quinH)(terpy)]-$(S_2O_8)_{0.5}$ the peaks are relatively narrow with FWHM values of 1.3—1.6 eV. The Ag(III) complexes exhibit radiation bleaching, whereas the Ag(II) and and Ag(I) complexes are stable to irradiation. Multiplet splitting patterns have been reported by Murtha and Walton [50]. The core bonding energies for the Ag(II) complexes $3d_{3/2}$ 372.9—375.1 eV and $3d_{5/2}$ 366.9—369 eV are very close to the silver(I) complexes 3*d* binding energies (373.8—374.5 and 368—368.6 eV) and do not permit a sensitive method of distinguishing silver-(II) from silver(I). The complex Ag(dipic)(dipicH$_2$) · 4 H$_2$O which is confirmed to be a distorted octahedron has the lowest 3*d* binding energies when compared directly to square planar Ag(bipy)$_2$S$_2$O$_8$ · H$_2$O and Ag(pic)$_2$. Possibly, in the higher coordinated species there is an increase of negative charge at the silver nuclei resulting in a decrease in metal electron binding energies and chemical shift.

The binding energy chemical shifts for Ag(III) complexes [73,83] 377—377.3 eV ($3d_{3/2}$) and 371—371.4 eV ($3d_{5/2}$) are substantial, indicative of the +3 oxidation state. These chemical shifts are some 3.0 eV greater than those for Ag(I) and Ag(II) complexes. In the Ag(III)OEP (ClO$_4$) spectrum the nitrogens are shifted to higher energies creating a partial positive charge. This is consistent with the greater electronegativity of Ag(III), causing an electron density shift from the N via a σ bond, which is not replaced by the poorly coupled π system.

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