

double-bond stretching frequency upon coordination for compounds of the type $\text{Ag}(\text{olefin})_2\text{BF}_4$. The reported values in cm^{-1} are 75, 62, 68, and 64. Failure to observe a correspondence between these shifts and the silver-olefin dissociation energies may be due to the different types of compounds being compared and/or to a number of theoretical reasons previously discussed.²⁴

All of the chemical shifts of the protons in an olefin experience a paramagnetic shift upon coordination to the silver ion. The shift becomes less as the carbon atoms become farther away from the metal. Thus the olefinic protons in the monoolefins are shifted downfield 0.59 ± 0.15 ppm when coordinated to the metal. The protons on the methylenic carbons next to the olefinic bond are shifted 0.25 ± 0.06 ppm, and those one carbon removed are shifted 0.10 ± 0.07 ppm. All of the protons in compounds of the type $\text{Ag}(\text{olefin})_2\text{BF}_4$ are similarly shifted relative to the uncoordinated olefin, 0.79 ± 0.10 ppm.²³ There is a correspondence between the chemical shifts of the coordinated olefinic protons and the relative dissociation energies (see Tables II and IV) but there is not between the shift of the chemical shift of the olefinic protons upon coordination and the relative dissociation energies. We have also found such a correspondence in the chelating olefinic compounds of the type $[\text{PdCl}_2(\text{olefin})]$ and $[\text{RhCl}(\text{olefin})_2]$ which will be reported elsewhere. Since theoretic

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cal calculations of chemical shifts in molecules are at a primitive stage of development, discussion on the reasons for the above correspondence is premature.

We observe that in all cases addition of excess olefin results in a lower enthalpic change when $[\text{Ag}(\text{hfacac})(\text{olefin})]$ is treated with triphenylphosphine (Table III, eq 3). We also observe a lower enthalpic change when increasing amounts of olefin are present. This is probably due to the formation of species of the type $[\text{Ag}(\text{hfacac})(\text{olefin})_2]$, which is not unexpected since similar silver olefin compounds exist.^{3,23} The dissociation energy of 1,5-cyclooctadiene is intermediate between cyclooctene and cyclohexene which suggests that only one double bond is coordinated or that on the average both double bonds coordinate more weakly than the monoolefins. The significance of the cyclooctatetraene enthalpic data cannot be discussed at this time due to its partially polymeric state in solution.

Registry No. $\text{P}(\text{C}_6\text{H}_5)_3$, 603-35-0; $[\text{Ag}(\text{hfacac})(\text{cyclopentene})]$, 38882-87-0; $[\text{Ag}(\text{hfacac})(\text{cyclohexene})]$, 38892-26-1; $[\text{Ag}(\text{hfacac})(\text{cycloheptene})]$, 38882-89-2; $[\text{Ag}(\text{hfacac})(\text{cis-cyclooctene})]$, 38882-85-8; $[\text{Ag}(\text{hfacac})(1,5\text{-cyclooctadiene})]$, 38892-25-0; $[\text{Ag}(\text{hfacac})(1,3,5,7\text{-cyclooctatetraene})]$, 37333-35-0; $[\text{Ag}(\text{hfacac})(\text{PPh}_3)]$, 38960-88-2; $[\text{Ag}(\text{hfacac})(\text{PPh}_3)_2]$, 26582-28-5.

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Contribution from the Department of Chemistry, Purdue University, Lafayette, Indiana 47907

Studies on Coordination Complexes of Silver(II). VIII.¹ Synthesis and Characterization of Mixed-Ligand Complexes of the Pyridinecarboxylic Acids and Other Nitrogen Heterocyclic Donor Molecules

D. P. MURTHA² and R. A. WALTON*

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When the silver(II) complex $\text{Ag}(\text{dipic})(\text{dipicH}_2) \cdot 4\text{H}_2\text{O}$ (dipicH_2 = pyridine-2,6-dicarboxylic acid) is allowed to react with 2,2',2''-terpyridyl, 2,2'-bipyridyl, or 1,10-phenanthroline in aqueous solution, the neutral terdentate ligand molecule dipicH_2 is readily replaced to yield mixed-ligand complexes of the general formula $\text{Ag}(\text{dipic})(\text{L}) \cdot x\text{H}_2\text{O}$. From the related reactions of other bis(pyridinecarboxylate) complexes of silver(II) with 1 mol of 2,2',2''-terpyridyl in the presence of diammonium peroxydisulfate, ionic derivatives of the general formula $\text{Ag}(\text{pyridinecarboxylate})(\text{terpy})(\text{S}_2\text{O}_8)_{1/2} \cdot x\text{H}_2\text{O}$ are formed. Infrared spectral studies and X-ray powder data provide good evidence for the formulation of these compounds as authentic mixed-ligand complexes. The physical properties and spectra of these compounds are discussed.

Introduction

The majority of silver(II) complexes which have been reported in the literature are four-coordinate species whose stereochemistry most probably approximates to square planar.³⁻¹¹ The very limited amount of unambiguous structural

information available for these complexes¹²⁻¹⁵ confirms an essentially square-planar structure. Morgan and Burstall previously reported the synthesis of several tris(2,2'-bipyridyl) complexes of silver(II)⁴ which were believed to be six-coor-

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Table I. Analytical Data and Magnetic Properties for the Silver(II)-Mixed-Ligand Complexes

Complex no.	Complex	% C		% H		% N		% S or Cl		% Ag		μ_{eff} , ^b BM	Temp, °K
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
1	Ag(dipic)(terpy)·4H ₂ O	45.69	45.74	3.84	4.16	9.69	9.53			18.65	18.98	2.14 (F)	297
2	Ag(dipic)(bipy)·3H ₂ O	42.25	42.73	3.55	3.58	8.70	8.64			22.32	22.14	1.88 (G)	298
3	Ag(dipic)(phen)·7/2H ₂ O	44.20	44.08	3.51	3.43	8.14	8.10			20.90	20.46	1.69 (G)	299
4	Ag(dipicH)(terpy)(S ₂ O ₈) _{1/2} ·2H ₂ O	41.33	41.67	3.00	3.13	8.76	8.84	5.02	5.63	16.87	17.10	1.82 (F)	297
5	Ag(pic)(terpy)(S ₂ O ₈) _{1/2} ·2H ₂ O	42.36	42.06	3.22	3.40	9.41	9.20	5.39	5.75	18.12	18.23	2.04 (F)	297
6	Ag(quinH)(terpy)(S ₂ O ₈) _{1/2}	43.80	43.53	2.51	2.49	9.29	9.05	5.31	5.58	17.88	17.65	1.82 (G)	298
7	Ag(lutH)(terpy)(S ₂ O ₈) _{1/2} ·H ₂ O	42.52	42.61	2.76	2.61	9.02	9.31	5.16	5.38	17.36	16.88	1.89 (G)	299
8	Ag(isocinchH)(terpy)(S ₂ O ₈) _{1/2} ^a	43.80	42.85	2.51	2.57	9.29	8.92	5.31	4.60	17.88	18.33	1.91 (G)	298
9	Ag(dipicH)(terpy)(ClO ₄)·2H ₂ O	41.11	41.53	2.98	3.11			5.52	5.71	16.78	16.84		

^a Analytical data indicate slight contamination by Ag(isocinchH)₂. ^b F, Faraday method; G, Gouy method.

dinate. However, recent work¹⁶ has cast doubt as to the existence of these derivatives.

The determination of the crystal structure of bis(pyridine-2,6-dicarboxylato)silver(II) monohydrate^{17,18} afforded the first unambiguous example of a truly six-coordinate silver(II) complex. Coordination about the central silver ion can best be described as a very distorted octahedron. However, the mode of coordination of the two ligand molecules is quite different. Coordination is achieved through a neutral pyridine-2,6-dicarboxylic acid ligand molecule (dipicH₂) and a dianionic ligand molecule (dipic). The metal-ligand bond lengths involving the former ligand moiety (dipicH₂) were significantly longer (by ca. 0.15 Å) than those associated with the dianionic ligand,^{17,18} implying that the former ligand molecule was more weakly held. This led us to suspect that this complex might undergo ligand substitution reactions with preferential replacement of the dipicH₂ molecule. Accordingly, we investigated several such reactions and in the present report describe our isolation and characterization of two groups of mixed-ligand complexes of silver(II), the first such derivatives of this oxidation state to have been isolated.

Experimental Section

Starting Materials. The following ligands were obtained from commercial sources and were used without further purification. Ligands are listed with their systematic and trivial names, together with their common abbreviations and commercial sources: (a) pyridine-2-carboxylic acid (picolinic acid), abbreviated picH, Aldrich Chemical Co.; (b) pyridine-4-carboxylic acid (isonicotinic acid), abbreviated isonichH, Eastman Organic Chemicals; (c) pyridine-2,3-dicarboxylic acid (quinolinic acid), abbreviated quinH₂, J. T. Baker Chemical Co.; (d) pyridine-2,4-dicarboxylic acid (lutidinic acid), abbreviated lutH₂, Aldrich Chemical Co.; (e) pyridine-2,5-dicarboxylic acid monohydrate (isocinchomeronic acid), abbreviated isocinchH₂, Aldrich Chemical Co.; (f) pyridine-2,6-dicarboxylic acid (dipicolinic acid), abbreviated dipicH₂, Aldrich Chemical Co.; (g) 2,2',2''-terpyridyl, abbreviated terpy, G. F. Smith Chemical Co.; (h) 2,2'-bipyridyl, abbreviated bipy, Aldrich Chemical Co.; (i) 1,10-phenanthroline monohydrate, abbreviated phen, Matheson Coleman and Bell.

Silver(II) Pyridinecarboxylates. Ag(quinH)₂·2H₂O, Ag(isocinchH)₂, Ag(dipic)(dipicH₂)·4H₂O, Ag(pic)₂, and Ag(isonic)₂·H₂O were prepared by standard literature procedures.^{8,10,13} The identity of these products was routinely established by a comparison of their infrared spectra with those reported in the literature. Ag(lutH)₂·2H₂O was prepared as described in part VII of this series.¹

Preparation of the Silver(II)-Mixed-Ligand Complexes. (i) Ag(dipic)(terpy)·xH₂O. Bis(pyridine-2,6-dicarboxylato)silver(II) tetrahydrate (1.114 g, 2.176 mmol) and 2,2',2''-terpyridyl (0.507 g, 2.176 mmol) were added to 35 ml of water whereupon the reaction mixture quickly turned from dark green to dark brown. The reaction was stirred for 45 min and then filtered. The precipitate was collected from the filter, stirred in 40 ml of water for 20 min, and once again

filtered. This second filtrate was combined with the original reaction filtrate and cooled in an ice bath. After approximately 2 hr, a small crop of needlelike crystals of the desired product was collected; yield 0.19 g, 15%. The crystals appeared dark green-black when wet but turned brown on drying.

Analytical data for this complex are given in Table I. However, for other preparative samples the analytical data were consistent with water of hydration intermediate between 2 and 3 mol. It appears that the water of hydration is variable for this complex. A comparison of the infrared spectra of the different hydrated forms showed them to be identical except for variations in the intensities of the vibrational frequencies associated with the water molecules.

(ii) Ag(dipic)(bipy)·3H₂O. Water (70 ml) was cooled in an ice bath (0–5°). Bis(pyridine-2,6-dicarboxylato)silver(II) tetrahydrate (0.50 g, 0.977 mmol) and 2,2'-bipyridyl (0.170 g, 1.088 mmol, 11% excess) were added to the cold water. The reaction mixture was stirred in the ice bath for 1.5 hr and filtered. The resulting brown product was washed with 50 ml of water and dried *in vacuo* over calcium chloride. It was then ground thoroughly, stirred in 60 ml of benzene for 5 min to ensure complete removal of excess bipyridyl, and redried; yield 0.313 g, 66%.

(iii) Ag(dipic)(phen)·7/2H₂O. This brown 1,10-phenanthroline complex was prepared using a similar procedure to that described above in (ii).

(iv) Ag(dipicH)(terpy)(S₂O₈)_{1/2}·2H₂O. Bis(pyridine-2,6-dicarboxylato)silver(II) tetrahydrate (1.44 g, 2.81 mmol), 2,2',2''-terpyridyl (0.659 g, 2.828 mmol), and diammonium peroxydisulfate (4.988 g, 21.88 mmol) were continuously stirred for 45 min in 60 ml of water. The brown precipitate was filtered, dried, and then stirred for 30 min in 200 ml of water which contained diammonium peroxydisulfate. This was then filtered and the filtrate was combined with the original reaction filtrate. The dark brown solution was placed in a refrigerator overnight, whereupon a small quantity of dark brown needles was obtained. These were washed with a few milliliters of water; yield 0.223 g, 12%.

This complex was also prepared by the reaction of equimolar proportions of Ag(terpy)S₂O₈·H₂O and pyridine-2,6-dicarboxylic acid in aqueous solution without the addition of diammonium peroxydisulfate. The reaction mixture was stirred for 1 hr and filtered, and the filtrate was cooled to produce crystals of the complex.

(v) Ag(dipicH)(terpy)(ClO₄)·2H₂O. 2,2',2''-Terpyridyl (0.201 g, 0.863 mmol) was added with stirring to 15 ml of distilled water and then mixed with an aqueous solution of sodium perchlorate (1.23 g in 15 ml, 10.08 mmol). Bis(pyridine-2,6-dicarboxylato)silver(II) tetrahydrate (0.44 g, 0.86 mmol) was then quickly added and the resulting brown reaction mixture was stirred for 1 hr. The crude product was filtered off and carefully washed with water (20 ml) and benzene. A portion of this product (0.20 g) was then purified by stirring with 75 ml of distilled water, whereupon most dissolved. The clear brown solution was stored in a refrigerator for 2 days and brown crystals of the desired product separated. These were filtered off and dried; yield 0.055 g.

(vi) **Other Complexes of the Type Ag(pyridinecarboxylate)(terpy)(S₂O₈)_{1/2}·xH₂O.** Complexes of this type were isolated with the following pyridinecarboxylic acids: picH, quinH₂, lutH₂, isocinchH₂. The appropriate pyridinecarboxylate complex of silver(II), 2,2',2''-terpyridyl,¹⁹ and an excess of diammonium per-

(16) W. G. Thorpe and J. K. Kochi, *J. Inorg. Nucl. Chem.*, **33**, 3598 (1971).

(17) Part II: M. G. B. Drew, G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Amer. Chem. Soc.*, **91**, 7769 (1969).

(18) Part IV: M. G. B. Drew, R. W. Matthews, and R. A. Walton, *J. Chem. Soc. A*, 1405 (1970).

(19) It is important in the synthesis of the ionic complexes to use only a very slight excess (1–3%) of 2,2',2''-terpyridyl. Larger amounts of this tertiary amine can lead to formation of the complex Ag(terpy)₂S₂O₈·3H₂O²⁰ or other undesirable side products.

(20) D. P. Murtha and R. A. Walton, unpublished work.

Table II. X-Ray Powder Data for Some Selected Silver(II) Compounds^a

Ag(pic) ₂ ^b	Ag(pic)(terpy)- (S ₂ O ₈) _{1/2} ·2H ₂ O	Ag(terpy) ₂ S ₂ O ₈ · 3H ₂ O	Ag(lutH)(terpy)- (S ₂ O ₈) _{1/2} ·H ₂ O	Ag(lutH) ₂ · 2H ₂ O
8.57 m ^c	7.98 s	11.79 m	10.36 w	10.63 s
6.73 vs	7.20 vs (asym)	9.56 vs (dbl)	8.51 m	6.58 vw
4.28 m	6.57 m	8.38 w (dbl)	7.30 s	6.00 mw
3.96 ms	6.10 m	7.22 mw	7.02 s	5.29 mw
3.70 ms	5.59 w	6.77 m	6.63 ms	4.99 mw
3.29 vw	5.27 mw	6.48 mw	6.14 mw	4.89 mw
3.20 vs	4.83 vw	6.18 mw	5.71 m	4.45 mw
3.09 m	4.67 w	5.86 mw	5.28 m	4.35 mw
2.86 w	4.41 m (dbl) ^d	5.25 w	4.98 mw	3.85 vw
2.73 w	4.11 m	5.10 vw	4.40 mw (br)	3.54 w
2.57 m	4.00 m	4.79 mw	4.06 m	3.33 w
2.43 m	3.75 ms	4.47 vw	3.91 m	3.16 s
2.32 m	3.65 mw (sh)	4.33 vw	3.70 mw	3.04 w
2.23 m	3.48 w	4.04 w	3.55 s (dbl)	2.95 w
2.08 w	3.37 m	3.95 w	3.36 s	2.80 w
1.97 mw	3.27 m (asym)	3.74 w	3.21 m	2.59 vw
	3.09 w	3.57 s	2.48 w	2.20 w
	3.00 vw	3.49 w	2.42 w	
	2.87 w	3.38 w (dbl)	2.30 w	
	2.75 vw	3.27 w	2.23 w	
		3.07 w	2.05 w	
		2.43 vw	1.99 w	

^a Interplanar (*d*) spacings are listed in angstroms, followed by their relative intensities. ^b These data are taken from ref 13. ^c Symbols used have the following meanings: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; br, broad; sh, shoulder; asym, asymmetric; dbl, doublet. ^d The listed *d* spacing is the midpoint of the doublet.

oxydisulfate were added simultaneously to water and the reaction mixture was stirred for 3 hr, during which time its color darkened considerably. The resulting brown product was filtered off, washed with water and then benzene, and dried *in vacuo* over calcium chloride.

The following quantities of reagents used in the preparation of Ag(pic)(terpy)(S₂O₈)_{1/2}·2H₂O illustrate this procedure: bis(pyridine-2-carboxylato)silver(II), 0.286 g, 0.812 mmol; 2,2',2''-terpyridyl, 0.189 g, 0.811 mmol; diammonium peroxydisulfate, 0.696 g, 3.05 mmol; volume of reaction solvent, 40 ml. The yield of product was 0.299 g, 62%.

Precautions. All the silver(II) products were stored in amber glass bottles and kept in a refrigerator to minimize decomposition. Their stabilities will be discussed later in this paper. Certain of the complexes may decompose (usually turning white) if exposed to infrared radiation for too long a period. Consequently, care should be exercised when running their infrared spectra.

Physical Measurements. Infrared spectra were recorded as Nujol mulls on a Beckman IR-12 spectrophotometer. Electronic absorption spectra were recorded for either aqueous solutions (~7 × 10⁻⁴ M) or as diffuse-reflectance spectra on a Cary 14 spectrophotometer equipped with a diffuse-reflectance attachment. Magnetic moments were determined by either the Gouy or Faraday methods using Hg[Co(SCN)₄] as the calibrant in each case. Corrections for the ligand diamagnetism were estimated from Pascal's constants. X-Ray powder photographs were taken with a Philips camera (Debye-Scherrer type) using a Cu Kα radiation (λ 1.5418 Å) and an exposure time of about 8 hr. Traces of the powder photographs were obtained using a Joyce double-beam recording microdensitometer.

Analytical Procedures. Silver was determined volumetrically using ammonium thiocyanate as the titrant and ferric ammonium sulfate as the indicator.²¹ All other analyses were performed by Dr. C. S. Yeh in the microanalytical laboratory of this department. Analytical data for the complexes described in this report are given in Table I.

Results and Discussion

The reaction of the silver(II) complex of pyridine-2,6-dicarboxylic acid, Ag(dipic)(dipicH₂)·4H₂O,^{17,18} with 2,2',2''-terpyridyl, 2,2'-bipyridyl, and 1,10-phenanthroline in aqueous solution affords mixed-ligand complexes of the type Ag(dipic)(L)·xH₂O (L = terpy, bipy, or phen). These derivatives (Table I) are the first mixed-ligand complexes of silver(II) to have been isolated. Of particular interest is the ability

of the six-coordinate complex Ag(dipic)(dipicH₂)·4H₂O to undergo ligand substitution reactions in aqueous solutions without resulting reduction to silver(I) species. Furthermore, the replacement of the more weakly bonded neutral dipicH₂ molecule rather than dipic supports our earlier description of this structure^{17,18} as one incorporating both neutral (dipicH₂) and dianionic (dipic) ligand molecules.

A further series of mixed-ligand complexes was prepared by treating the appropriate bis(pyridinecarboxylate) of silver(II)^{7,8,10} with an equimolar proportion of 2,2',2''-terpyridyl in an aqueous solution of diammonium peroxydisulfate. Under these conditions ionic derivatives of the type Ag(pyridinecarboxylate)(terpy)(S₂O₈)_{1/2}·xH₂O were isolated (Table I). By the use of sodium perchlorate in place of diammonium peroxydisulfate, the perchlorate salt Ag(dipicH)(terpy)ClO₄·2H₂O was isolated but S₂O₈²⁻ was the preferred anion for stabilizing these species.

Confirmation that the above ionic derivatives were not 1:1 mixtures of previously characterized neutral and ionic silver(II) complexes was provided by X-ray powder measurements on Ag(pic)(terpy)(S₂O₈)_{1/2}·2H₂O and Ag(lutH)(terpy)(S₂O₈)_{1/2}·H₂O (Table II). From the *d* spacings and relative intensities (particularly at low 2θ values) it is clear that these two complexes are not the mixtures Ag(pic)₂-Ag(terpy)₂-S₂O₈·3H₂O and Ag(lutH)₂·2H₂O-Ag(terpy)₂S₂O₈·3H₂O, respectively; these mixtures could, of course, have satisfactorily explained the analytical data (Table I). Furthermore, the infrared spectra of all the complexes in the region 4000-600 cm⁻¹ indicate the existence of discrete mixed-ligand complexes since the spectra are quite different from those obtained by a superimposition of the spectra of the appropriate parent pyridinecarboxylate complex of silver(II)¹⁰ and Ag(terpy)₂S₂O₈·3H₂O.²⁰ The infrared spectra of the new complexes are now considered in more detail.

Infrared Spectra. Spectral data for the regions 3700-3100 and 1800-1600 cm⁻¹ are presented in Table III. The conversion of Ag(dipic)(dipicH₂)·4H₂O to complexes 1, 2, and 3 (Table I) is accompanied by the disappearance of prominent absorptions in the 1750-1700-cm⁻¹ region. In the spectrum of Ag(dipic)(dipicH₂)·4H₂O, bands at 1730 (sh)

(21) A. I. Vogel, "Quantitative Inorganic Analysis," Longmans, Green and Co., New York, N. Y., 1961, p 264.

Table III. Infrared Spectra of the Silver(II) Complexes in the Regions 3700–3100 and 1800–1600 cm^{-1}

Complex no.	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{O})$ of $-\text{CO}_2\text{H}$	$\nu_{\text{as}}(\text{C}-\text{O})$ of $-\text{COO}^-$
1	3370–3260 s, br		~1650 sh, 1610 s
2	~3410 m, br	1732 w, 1717 w?	1632 s, ~1617 s, sh, ~1605 s, sh
3	~3410 ms, br	~1730 w, sh, ~1700 w, sh?	~1620 s, br
4	~3450 m, br	~1730 m, br	1673 ms
5	~3510 m, sh, ~3400 m, br, ~3310 m, br		1650 m, 1617 s
6		~1712 mw	
7	~3555 mw, ~3495 mw, ~3400 w, sh	1723 s	1651 m, 1630 s, 1601 ms
8		1717 ms	~1605 sh
9	~3600 m	1716 mw, br	1632 m

and 1705 (m) cm^{-1} are assigned to $\nu(\text{C}=\text{O})$ of the dipicH₂ moiety.¹⁰ Replacement of this ligand by 2,2',2''-terpyridyl, 2,2'-bipyridyl, and 1,10-phenanthroline results in loss of the 1705- cm^{-1} band. For the 2,2'-bipyridyl and 1,10-phenanthroline complexes, weak residual absorptions in this region (Table III) are not considered significant. Strong $\nu_{\text{asym}}(\text{COO})$ bands are still present in the infrared spectra of these complexes near 1650–1600 cm^{-1} .

For the ionic derivatives containing "free" acid groups (complexes 4 and 6–9), the prominent absorption band between 1750 and 1700 cm^{-1} (Table III) is assigned to $\nu(\text{C}=\text{O})$ of $-\text{COOH}$.¹⁰ As expected, no such band is present in the spectrum of the pyridine-2-carboxylate complex 5. This observation, coupled with the absence of bands characteristic of the terpyridinium cation,²² confirms our formulation of these complexes as in Table I, rather than the alternative such as $\text{Ag}(\text{dipic})(\text{terpyH})(\text{S}_2\text{O}_8)_{1/2} \cdot 2\text{H}_2\text{O}$. In addition to the absorption bands arising from the coordinated nitrogen heterocyclic molecules, complexes 4–8 exhibited bands characteristic of ionic peroxydisulfate:²³ ~1280–1260 (vs, br), 1047–1046 (ms), 698–690 (m, br) cm^{-1} . For the perchlorate derivative, complex 9, the characteristic ν_3 absorption band of the perchlorate anion was located at ~1105 cm^{-1} .

Electronic Absorption Spectra and Magnetic Properties.

The diffuse-reflectance spectrum of $\text{Ag}(\text{dipic})(\text{terpy}) \cdot 4\text{H}_2\text{O}$ has a well-defined band at 14,400 cm^{-1} which is certainly a $d \leftrightarrow d$ transition. However, the related spectrum of $\text{Ag}(\text{dipicH})(\text{terpy})(\text{S}_2\text{O}_8)_{1/2} \cdot 2\text{H}_2\text{O}$ showed only a broad, rising absorption in this region and no definite peaks or shoulders were observed. Both of these compounds, as well as complex 9, exhibit similar electronic spectra in aqueous solution (Figure 1) with the maximum ~15,200 cm^{-1} (ϵ_{max} 240–250) assigned as a $d \leftrightarrow d$ ligand field band. This probably indicates the formation of a common species in water. The aqueous solution spectrum of $\text{Ag}(\text{dipic})(\text{dipy}) \cdot 3\text{H}_2\text{O}$ (compound 2) exhibits a very broad ligand field band centered at 13,100 cm^{-1} . Rapid decomposition of the solution during the scan prevented an accurate determination of ϵ_{max} . The related phenanthroline complex 3 had a similar solution spectrum to that of 2.

Low-energy $d \leftrightarrow d$ transitions were found for $\text{Ag}(\text{dipic})(\text{dipicH}_2) \cdot 4\text{H}_2\text{O}$ at 16,700 cm^{-1} in its diffuse-reflectance spectrum and at 17,400 and 11,000 cm^{-1} in its aqueous solution spectrum.¹⁸ Since the lowest energy ligand field transitions for planar silver(II) complexes invariably occur in the region from 20,000 to 25,000 cm^{-1} ,^{6,10,24,25} it seems likely that the mixed-ligand complexes mentioned above have distorted five- or six-coordinate structures. However, higher

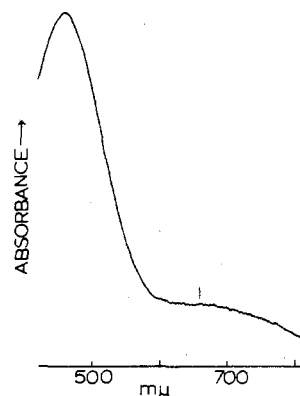


Figure 1. Electronic absorption spectrum of an aqueous solution of $\text{Ag}(\text{dipicH})(\text{terpy})\text{ClO}_4 \cdot 2\text{H}_2\text{O}$ ($7.47 \times 10^{-4} M$).

coordination numbers cannot be ruled out at present.

There is a well-defined intense absorption (ϵ_{max} 1230–1360) in the aqueous solution spectra of all silver(II)-mixed-ligand complexes containing the 2,2',2''-terpyridyl ligand. This band also appears in the diffuse-reflectance spectra, usually as a shoulder. Although the nature of this band is not known with certainty, it most probably arises from a modified intraligand transition of 2,2',2''-terpyridyl or a $\text{Ag}(d) \rightarrow \text{terpy}(\pi^*)$ electron-transfer transition. It is believed that the presence of this band obscures (in some cases) any $d \leftrightarrow d$ ligand field transitions which occur below 20,000 cm^{-1} .

It is noteworthy that the diffuse-reflectance spectra of the present series of mixed-ligand compounds showed a broad, continuously rising absorption from the beginning of the scan (8500 cm^{-1}). In contrast, the diffuse-reflectance spectra of several representative planar four-coordinate silver(II) complexes, e.g., $\text{Ag}(\text{bipy})_2\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}^+$ and $\text{Ag}(\text{terpy})\text{S}_2\text{O}_8 \cdot \text{H}_2\text{O}$,²⁰ which we also recorded, showed a decreasing absorbance until ~13,000 cm^{-1} and only then began to rise sharply. This indicates that low-energy ligand field bands are present in the mixed-ligand complexes but are unresolved.

Room-temperature magnetic moments for the series of silver(II) chelates are listed in Table I. No attempt was made to correct these values for temperature-independent paramagnetism. Measurements were made mainly to establish the paramagnetic nature of the complexes. Due to the relatively small weight changes occurring during measurement, the likely error in μ_{eff} is at least ± 0.1 BM.

As expected,¹⁰ most of the compounds have magnetic moments slightly above the spin-only value for one unpaired electron. It is apparent from the results that no significant magnetic exchange occurs at room temperature. The moments reported in Table I are consistent with the values previously found for other silver(II) complexes.¹⁰

Stability of the Mixed-Ligand Complexes. With the exception of complex 7, the mixed-ligand complexes were stable for at least several months in the solid state if stored as described in the Experimental Section. The decomposition

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of 7 was noticeable after 2-3 days and could be followed by infrared spectroscopy in the 3600-3400- and 1800-1500- cm^{-1} regions. For instance, the band at 1723 cm^{-1} (ν -C=O) of -COOH decreased in intensity with time, while a band at 1651 cm^{-1} , formerly the weakest band for a freshly prepared sample in this spectral region, became much more intense. These changes could be explained by the change from "free" -COOH to -COOAg which accompanied the decomposition.

The new compounds described in this report all show at least limited solubility in water to form brown solutions, with complexes 1, 4, and 9 being the most soluble of the series. These solutions are remarkable in their stability toward water reduction to silver(I) species, especially the mixed dipic-terpy complexes. It has previously been noted that aqueous solutions of silver(II) compounds^{18,24} show drastic decompositions of 25-50% or greater after only a couple of hours. Some measure of the enhanced stability of certain of the complexes described in the present report is the observation that an aqueous solution of Ag(dipicH)(terpy)-(S₂O₈)_{1/2}·2H₂O (5.9 × 10⁻⁴ M) still retained some characteristic silver(II) color after 3 months. Apparently, the solu-

bility and/or stability of the mixed-ligand complexes in water is enhanced by two factors: (1) their higher coordination number as contrasted with most silver(II) species and (2) the strong stabilizing influence of 2,2',2''-terpyridyl in these complexes.

Registry No. Ag(dipic)(terpy)·4H₂O, 12799-09-6; Ag(dipic)(bipy)·3H₂O, 12799-06-3; Ag(dipic)(phen)·7/2H₂O, 12799-07-4; [Ag(dipicH)(terpy)][S₂O₈]_{0.5}, 12799-10-9; [Ag(pic)(terpy)][S₂O₈]_{0.5}·2H₂O, 37337-85-2; [Ag(quinH)(terpy)][S₂O₈]_{0.5}, 12799-11-0; [Ag(lutH)(terpy)][S₂O₈]_{0.5}, 12799-12-1; [Ag(isocinchH)(terpy)][S₂O₈]_{0.5}, 12799-13-2; [Ag(dipcH)(terpy)]ClO₄, 37337-86-3; [Ag(terpy)₂][S₂O₈]·3H₂O, 37337-87-4; Ag(lutH)₂·2H₂O, 36926-56-4; Ag(dipic)(dipicH₂)·4H₂O, 36900-76-2; 2,2'-bipyridyl, 366-18-7; Ag(terpy)₂S₂O₈, 12565-92-3; Ag(pic)₂, 14783-00-7.

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Contribution from Bell Laboratories,
Murray Hill, New Jersey 07974

Mercury-201 Nuclear Quadrupole Resonance.

I. Mercury and Halogen Nqr in the Mercuric Halide Dioxanates

D. B. PATTERSON,* G. E. PETERSON, and A. CARNEVALE

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²⁰¹Hg and halogen nqr have been observed in the 1:2 complexes of mercuric chloride and bromide with 1,4-dioxane. Since some confusion has arisen in the literature as a result of failure to distinguish between the 1:2 and 1:1 mercuric chloride-dioxane complexes, the reported halogen resonances of the 1:1 dioxane complexes of mercuric chloride, bromide, and iodide were verified. Additionally, the $\pm 3/2 \leftrightarrow \pm 5/2$ transition for ¹²⁷I in the 1:1 mercuric iodide complex was observed and its frequency measured. No ²⁰¹Hg nqr was observed in any of the 1:1 complexes or in mercuric bromide itself although the apparently only other known ²⁰¹Hg nqr frequency, that of mercuric chloride, was confirmed. The changes in the halogen and mercury nqr frequencies upon complexation are interpreted, employing the usual Townes-Dailey approach, in terms of the effects of substituting oxygen for halogen in the highly distorted octahedral coordination about mercury which is found in all the compounds herein.

Introduction

In 1954, Dehmelt, Robinson, and Gordy reported the ²⁰¹Hg ($I = 3/2$) nuclear quadrupole resonance (nqr) frequency for mercuric chloride, as well as the chlorine frequencies.¹ That report apparently remains the only observation of ²⁰¹Hg nqr until the present work. Other, unspecified, mercury compounds were examined by the previous workers but without success.

At the initiation of a program of ²⁰¹Hg nqr, we turned to the mercuric halide dioxanates since the available structural data, *i.e.*, the X-ray structure determination of the 1:1 complex of mercuric chloride with 1,4-dioxane² and that of the 1:2 complex of mercuric bromide with this ligand,³ indicate that the mercuric chloride complexes should represent fairly weak perturbations of the one system in which ²⁰¹Hg nqr

had been observed. Furthermore, the 1:2 complexes represent an instance in which linear HgX₂ units are isolated from one another in the solid state, unlike the halides themselves in which intermolecular mercury-halogen coordination occurs to varying degrees. Thus a more direct comparison of mercury-halogen covalent bonds, uncomplicated by mercury-halogen coordination, might be obtained from measurements on these complexes. Finally, halogen nqr had already been observed in many of these complexes.⁴⁻⁶

Of the six complexes in this set, the 1:1 and 1:2 complexes of mercuric chloride, bromide, and iodide with 1,4-dioxane, all are known compounds except for the 1:2 complex of mercuric iodide and we have been unable to obtain any evidence that it exists at room temperature. The mercuric iodide-dioxane system is thus straightforward but the existence of (at least) two distinct complexes for each of the other

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