

(i) **Preparation of  $[\text{Pt}(\text{CH}_3)_3[\text{As}(\text{CH}_3)_3]_2(\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O})] \cdot (\text{PF}_6)_2$ .**  $\text{AgPF}_6$  (0.079 g, 0.312 mmol) was added to a solution of  $\text{Pt}(\text{CH}_3)_3[\text{As}(\text{CH}_3)_3]_2\text{I}$  (0.190 g, 0.312 mmol) in 10 ml of acetone. The AgI was removed by centrifuge to give a clear colorless solution. 1-Butyn-4-ol (0.312 mmol) was added, the solution was stirred for 10 min, and the solvent was removed on a rotary evaporator to give a white solid that was recrystallized from dichloromethane and ether to give white needles; 85% yield. The crystals slowly darkened and decomposed over a period of a few hours even when stored under nitrogen.

(j) **Pyrolysis of  $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{Q}_2\text{I}$ .** A 0.100-g amount of  $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{Q}_2\text{I}$  was placed in the bottom of a 25-ml round-bottom flask. The flask was evacuated and the bottom was placed in the preheated oil bath at 165°. Effervescence immediately occurred leaving a white solid. The evolved gases were analyzed by mass spectrometry and infrared spectroscopy. The solid residue was then recrystallized from methanol to give white needles. The nmr spectrum was recorded and the platinum methyl peak was integrated against those of the phosphine methyls.

**Registry No.** *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{NC}_5\text{H}_5)](\text{PF}_6)$ , 37081-49-5; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_3](\text{PF}_6)$ , 37081-50-8; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2\text{-P}(\text{OCH}_3)_3][\text{B}(\text{Ph})_4]$ , 37035-91-9; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2\{\text{Sb}(\text{CH}_3)_3\}](\text{PF}_6)$ , 37035-92-0; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_6\text{H}_4\text{CH}_3)](\text{PF}_6)$ , 37081-51-9; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_6\text{H}_4\text{OCH}_3)](\text{PF}_6)$ , 37035-93-1; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNCH}_3)][\text{B}(\text{Ph})_4]$ , 37035-94-2; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}_2(\text{CNC}_2\text{H}_5)](\text{PF}_6)$ , 37035-95-3; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{A}_2(\text{NCC}_6\text{F}_5)](\text{PF}_6)$ , 37035-96-4; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{A}_2\text{Q}](\text{PF}_6)$ , 37035-97-5; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{A}_2(\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O})](\text{PF}_6)$ , 37035-82-8; *fac*- $[\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_3](\text{PF}_6)$ , 37408-40-5; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}(\text{CNC}_6\text{H}_4\text{CH}_3)_2](\text{PF}_6)$ , 37036-88-7; *fac*- $[\text{Pt}(\text{CH}_3)_3\text{Q}(\text{NC}_5\text{H}_5)_2](\text{PF}_6)$ , 37036-89-8; *fac*- $\text{Pt}(\text{CH}_3)_3\text{A}_2\text{I}$ , 36604-67-8; *fac*- $\text{Pt}(\text{CH}_3)_3\text{Q}_2\text{I}$ , 24833-69-0;  $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{A}_2\text{I}$ , 37036-92-3;  $\text{Pt}(\text{CH}_3)_2(\text{CD}_3)_2\text{Q}_2\text{I}$ , 37036-93-4; *fac*- $\text{Pt}(\text{CH}_3)_3(\text{CNC}_6\text{H}_4\text{CH}_3)_2\text{I}$ , 37036-94-5; *trans*- $[\text{Pt}(\text{CH}_3)_2\text{Q}_2(\text{CO})][\text{B}(\text{Ph})_4]$ , 37036-95-6; *cis*- $\text{Pt}(\text{CH}_3)_2\text{Q}_2$ , 24917-48-4; *cis*- $\text{Pt}(\text{CH}_3)_2\text{A}_2$ , 15413-98-6;  $\text{CD}_3\text{I}$ , 865-50-9.

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## Studies on Coordination Complexes of Silver(II). VII.<sup>1</sup> A Comparative Study of the X-Ray Photoelectron Spectra of Complexes of Silver(II) and Silver(I) Containing Nitrogen Donor Molecules. Silver 3d and Nitrogen 1s Binding Energies

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The X-ray photoelectron spectra of twenty-five coordination complexes of silver(I) and silver(II) have been investigated and the silver 3d<sub>3/2</sub> and 3d<sub>5/2</sub> binding energies measured. While these binding energies show little variation with changes in formal oxidation state, their peak widths are usually broader by at least 0.8 eV for the paramagnetic silver(II) species, a feature which may be due in part to the occurrence of "multiplet splittings." Within the series of silver(II) complexes, there is some evidence for the dependence of silver 3d binding energies upon coordination number. Nitrogen 1s binding energies have been recorded for several of the complexes, with the object of assisting in the characterization of "silver(I) picolinate," a compound of ill-defined stoichiometry. The preparations of the new complexes bis(isoquinoline-1-carboxylato)silver(II) and pyridine-2,6-dicarboxylatodisilver(I) monohydrate are described.

### Introduction

The technique of X-ray photoelectron spectroscopy (ESCA<sup>3</sup>) has recently been applied to a study of compounds of the heavier transition elements with the principal object of establishing whether correlations exist between electron binding energies and the formal charge at the metal center. To date, most detailed studies have been carried out on coordination complexes of platinum and palladium, where fairly extensive series of complexes are available for study.<sup>4-7</sup>

The results generally bear out the expected trends: (a) a decrease in the binding energies of metal core electrons with decrease in oxidation state; (b) a dependence of these binding energies upon ligand electronegativities and  $\pi$ -acceptor ability. Unfortunately, for the heavier transition elements, there is often unlikely to be a clear correlation between a "characteristic" range of binding energies and a particular oxidation state. This is illustrated by the similar molybdenum 3d<sub>3/2</sub> and 3d<sub>5/2</sub> binding energies of  $\text{MoCl}_4 \cdot 2\text{py}$  and  $\text{MoO}_2(\text{acac})_2$ , derivatives of molybdenum(IV) and -(VI), respectively,<sup>8</sup> and the similar iridium 4f<sub>5/2</sub> and 4f<sub>7/2</sub> binding energies of  $[\text{Ir}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $[\text{Me}_3\text{N}]_2\text{IrCl}_6$ .<sup>9</sup> However, generally it seems that the higher the oxidation states, the greater is the binding energy difference, provided comparisons are made within related series of compounds.

Many of the chemical problems of current interest to us involve a study of low oxidation state transition metal complexes and we have consequently been interested in the X-ray photoelectron spectra of such species. Specifically we have

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investigated the spectra of a variety of complexes of rhodium, silver, and rhenium and in the present report we present the results of an investigation of the silver 3d binding energies of 25 coordination complexes of silver(I) and silver(II). The purposes of this study were as follows: (a) to establish whether these binding energies follow the usual trend with change in oxidation state and thereby enable a check to be made for silver(I) contaminants in the highly oxidizing silver(II) species; (b) to compare peak widths between diamagnetic  $d^{10}$  silver(I) complexes and the paramagnetic  $d^9$  silver(II) derivatives; (c) to establish whether the binding energies show any clear dependence upon coordination number.

## Experimental Section

**Starting Materials.** The following ligand molecules used in this study were obtained from the sources stated below. Their systematic and trivial names (where appropriate) are also given, together with their common abbreviations: (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) isoquinoline-1-carboxylic acid, abbreviated isoquin-1-COOH, Aldrich Chemical Co.; (d) pyridine-2,3-dicarboxylic acid (quinolinic acid), abbreviated quinH<sub>2</sub>, J. T. Baker Chemical Co.; (e) pyridine-2,4-dicarboxylic acid (lutidinic acid), abbreviated lutH<sub>2</sub>, Aldrich Chemical Co.; (f) pyridine-2,5-dicarboxylic acid monohydrate (isocinchomeronic acid), abbreviated isocinchH<sub>2</sub>, Aldrich Chemical Co.; (g) pyridine-2,6-dicarboxylic acid (dipicolinic acid), abbreviated dipicH<sub>2</sub>, Aldrich Chemical Co.; (h) pyridine-3,4-dicarboxylic acid (cinchomeronic acid), abbreviated cinchH<sub>2</sub>, Aldrich Chemical Co.; (i) 2,2'-bipyridyl, abbreviated bipy, Aldrich Chemical Co.; (j) 1,10-phenanthroline, abbreviated phen, Matheson Coleman and Bell.

Samples of pyrazine-2-carboxylic acid, pyrazine-2,3-dicarboxylic acid, and pyrazine-2,3,5-tricarboxylic acid dihydrate were kindly provided by Dr. Raymond W. Matthews.<sup>10</sup>

(a) **Preparation of Silver(I) Complexes.** The silver(I) complexes of pyrazine-2-carboxylic acid, pyrazine-2,3-dicarboxylic acid, and pyrazine-2,3,5-tricarboxylic acid were prepared as described previously.<sup>11</sup>

(i) **Pyridine-2,6-dicarboxylato silver(I) Monohydrate.** The white complex Ag<sub>2</sub>(dipic)·H<sub>2</sub>O precipitated on mixing aqueous solutions of excess silver nitrate (0.76 g) and neutralized pyridine-2,6-dicarboxylic acid (0.30 g); a 2:5 to 1:0 ratio of AgNO<sub>3</sub> to acid was used. The reaction mixture was stirred for 1 hr in the absence of light and filtered and the white product washed with 40 ml of distilled water and dried *in vacuo* over calcium chloride in a covered desiccator; yield 0.54 g. *Anal.* Calcd for C<sub>8</sub>H<sub>8</sub>AgNO<sub>5</sub>: C, 21.1; H, 1.2; Ag, 54.1; N, 3.5. Found: C, 20.75; H, 1.4; Ag, 54.2; N, 3.15. Characteristic infrared absorption bands include the following (cm<sup>-1</sup>): 3700-3100 (ν(O-H)); ~1610 (s, br) and ~1570 (vs, br) (ν(C-O)).

(ii) **Bis(2,2'-bipyridyl)silver(I) Nitrate Dihydrate.** Silver nitrate (1.20 g) and 2,2'-bipyridyl (2.20 g) were added to 175 ml of 50% aqueous ethanol and the reaction mixture was boiled for 5 min. The solution was allowed to cool to room temperature and the resulting yellow needles of Ag(bipy)<sub>2</sub>NO<sub>3</sub>·2H<sub>2</sub>O were collected and washed with a small volume of water. The product was then recrystallized twice from hot 50% aqueous ethanol and dried *in vacuo*; yield 0.98 g. *Anal.* Calcd for C<sub>20</sub>H<sub>20</sub>AgN<sub>5</sub>O<sub>5</sub>: C, 46.35; H, 3.9; Ag, 20.8; N, 13.5. Found: C, 45.9; H, 4.0; Ag, 20.7; N, 13.1.

Previous literature reports<sup>12-15</sup> have formulated this complex as the anhydrous derivative. Different preparative techniques and drying procedures could account for these hydration differences. For the dihydrate, we find the following characteristic infrared absorption bands (Nujol mull) in the 4000-1550 cm<sup>-1</sup> region: 3700-3150 (br) (ν(O-H)); ~1635 (w, br) (δ(O-H)); 1593 (m); 1586 (m); 1575 (mw); 1566 (m).

(iii) **Bis(1,10-phenanthroline)silver(I) Nitrate Monohydrate.**

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This complex which has been previously reported<sup>16,17</sup> was prepared by us by a procedure similar to that described above for the 2,2'-bipyridyl complex. *Anal.* Calcd for C<sub>24</sub>H<sub>18</sub>AgN<sub>5</sub>O<sub>4</sub>: C, 52.6; H, 3.3. Found: C, 52.05; H, 3.3.

(iv) **The Attempted Isolation of a Silver(I) Complex of Pyridine-2-carboxylic Acid.** The product which formed upon reaction of silver nitrate with pyridine-2-carboxylic acid appeared to be critically dependent upon the pH of the solution.

**Procedure 1.** Pyridine-2-carboxylic acid (1.87 g) was dissolved in 175 ml of distilled water (adjusted to pH 3-4) and silver nitrate (3.20 g) in a few milliliters of distilled water was added, whereupon a white gelatinous precipitate separated. The reaction mixture was stirred for 45 min in a covered beaker and filtered, the insoluble product was washed freely with distilled water and then dried *in vacuo* over calcium chloride in a covered desiccator; yield 1.40 g. *Anal.* Found (for duplicate preparative samples): C, 31.1, 31.2; H, 2.9, 2.8; Ag, 35.6, 35.7; N, 7.5, ... Although the analytical data were reproducible, they did not appear to fit any obvious stoichiometric formulation, such as Ag(pic). The infrared spectrum of this product showed a normal ν(C-O) carboxylate absorption<sup>11,18</sup> at 1589 (s) cm<sup>-1</sup> and, in addition, absorptions at ~1682 (s) cm<sup>-1</sup> and from 2600 to 2200 (mw, br) cm<sup>-1</sup> characteristic of ν(C-O) and hydrogen-bonded ν(O-H) of a carboxylic acid group. However, the analytical data ruled out a formulation such as Ag(picH)NO<sub>3</sub>.

This low-pH form reacts with 2,2'-bipyridyl and 1,10-phenanthroline to form the complexes Ag(bipy)<sub>2</sub>NO<sub>3</sub>·2H<sub>2</sub>O and Ag(phen)<sub>2</sub>NO<sub>3</sub>·H<sub>2</sub>O in low yield. *Anal.* Calcd for C<sub>20</sub>H<sub>20</sub>AgN<sub>5</sub>O<sub>5</sub>: C, 46.35; H, 3.9; Ag, 20.8; N, 13.5. Found: C, 45.2; H, 3.9; Ag, 22.05; N, 12.7. The phenanthroline complex was identified by infrared spectroscopy.

**Procedure 2.** Using a procedure similar to 1 but adjusting the pH to 7, afforded 0.55 g of white insoluble product from 0.81 g of silver nitrate. *Anal.* Found: C, 25.65; H, 2.3; Ag, 45.5; N, 7.7. Carboxylate absorptions at 1561 (s), 1579 (s), and 1604 (ms) cm<sup>-1</sup> were located in the infrared spectrum of this product, which differed appreciably from that of the product from procedure 1. However, as in the latter case, reaction with 2,2'-bipyridyl produced Ag(bipy)<sub>2</sub>NO<sub>3</sub>·2H<sub>2</sub>O in low yield.

(b) **Preparation of Silver(II) Complexes.** The following silver(II) complexes were prepared by literature methods: Ag(pic)<sub>2</sub>,<sup>19</sup> Ag(isonic)<sub>2</sub>·H<sub>2</sub>O,<sup>18</sup> Ag(quinH)<sub>2</sub>·2H<sub>2</sub>O,<sup>20</sup> Ag(isocinchH)<sub>2</sub>,<sup>20</sup> Ag(cinchH)<sub>2</sub>·H<sub>2</sub>O,<sup>18</sup> and Ag(dipic)(dipicH<sub>2</sub>)·4H<sub>2</sub>O.<sup>18</sup> The mixed silver(I)-silver(II) complex of pyrazine-2,3-dicarboxylic acid, Ag<sub>2</sub>Ag<sup>II</sup>(pyz-2,3-COO)<sub>2</sub>, was prepared by a slight modification of our original procedure.<sup>11</sup>

The synthesis and characterization of the following new silver(II) complexes, whose X-ray photoelectron spectra are reported here, are described in part VIII of this series:<sup>1b</sup> Ag(dipic)(terpy)·4H<sub>2</sub>O (terpy = 2,2',2''-terpyridyl); Ag(dipic)(bipy)·3H<sub>2</sub>O; Ag(dipic)(phen)·7/2H<sub>2</sub>O; [Ag(L)(terpy)](S<sub>2</sub>O<sub>8</sub>)<sub>0.5</sub>·xH<sub>2</sub>O, where L = dipicH, quinH, lutH, isocinchH, and pic.

(i) **Bis(pyridine-2,4-dicarboxylato)silver(II) Dihydrate.** The procedure of Banerjee and Ray<sup>20</sup> was followed but with an increased ratio of acid to silver nitrate (1.7:1.0). Furthermore, we used diammonium peroxydisulfate rather than the sodium salt. Our method afforded the dihydrate rather than the anhydrous<sup>20</sup> complex. *Anal.* Calcd for C<sub>14</sub>H<sub>12</sub>AgN<sub>2</sub>O<sub>10</sub>: C, 35.3; H, 2.5; Ag, 22.7; N, 5.9. Found: C, 35.2; H, 2.45; Ag, 22.2; N, 5.7. The magnetic moment of this complex was 1.81 BM at 299°K as determined by the Gouy technique.

(ii) **Bis(2,2'-bipyridyl)silver(II) Peroxydisulfate Monohydrate.** This known complex<sup>13</sup> was prepared from the low-pH form of "silver(I) picolinate" (see preparation (a)(iv)). The latter product (0.355 g), 2,2'-bipyridyl (0.52 g), and diammonium peroxydisulfate (4.345 g) were added to 100 ml of distilled water and the reaction mixture was stirred for 2 hr. The brown insoluble product was filtered off, washed well with distilled water (150 ml) and benzene (150 ml), and dried *in vacuo* over calcium chloride; yield 0.895 g. *Anal.* Calcd for C<sub>20</sub>H<sub>18</sub>AgN<sub>4</sub>O<sub>8</sub>S<sub>2</sub>: C, 38.1; H, 2.9; Ag, 17.1; N, 8.9. Found: C, 38.25; H, 3.0; Ag, 16.8; N, 8.65. In addition to the presence of characteristic 2,2'-bipyridyl and ionic S<sub>2</sub>O<sub>8</sub><sup>2-</sup> absorption bands in the infrared spectrum of this complex, sharp intense bands at 3560 and 3490 cm<sup>-1</sup>

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Table I. Silver 3d and Nitrogen 1s Binding Energies of Coordination Complexes of Silver(I) and Silver(II)<sup>a</sup>

Compound	No.	Ag 3d <sub>3/2</sub>	Ag 3d <sub>5/2</sub>	N 1s	
Ag(bipy) <sub>2</sub> NO <sub>3</sub> ·2H <sub>2</sub> O	1	374.1	368.1	406.2	399.3
Ag(phen) <sub>2</sub> NO <sub>3</sub> ·H <sub>2</sub> O	2	374.1	368.1	406.3	399.6
"Ag(pic)," low-pH form	3	374.1	368.1	406.0	399.6
"Ag(pic)," high-pH form	4	374.4	368.2		399.9
Ag <sub>2</sub> (dipic)·H <sub>2</sub> O	5	374.5	368.5		399.4
Ag(pyzoCOO)	6	374.1	368.0		399.9
Ag <sub>2</sub> (pyz-2,3-(COO) <sub>2</sub> )	7	374.2	368.2		
Ag <sub>3</sub> (pyz-2,3,5-(COO) <sub>3</sub> )·H <sub>2</sub> O	8	374.1	368.2		
Ag <sup>I</sup> <sub>2</sub> Ag <sup>II</sup> (pyz-2,3-(COO) <sub>2</sub> ) <sub>2</sub>	9	374.1	368.1		
Ag(bipy) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ·H <sub>2</sub> O	10	373.9	368.0		
Ag(pic) <sub>2</sub>	11	374.2	368.0		
Ag(isonic) <sub>2</sub> ·H <sub>2</sub> O	12	373.9	367.9		
Ag(isoquin-1-COO) <sub>2</sub>	13	374.1	368.0		
Ag(quinH) <sub>2</sub> ·2H <sub>2</sub> O	14	373.6	367.6		
Ag(isocinchH) <sub>2</sub>	15	375.1	369.0		
Ag(lutH) <sub>2</sub> ·2H <sub>2</sub> O	16	374.1	368.2		
Ag(cinchH) <sub>2</sub> ·H <sub>2</sub> O	17	374.5	368.5		
Ag(dipic)(dipicH <sub>2</sub> )·4H <sub>2</sub> O	18	372.9	366.9		398.5
Ag(dipic)(bipy)·3H <sub>2</sub> O	19	373.6	367.7		398.8
Ag(dipic)(phen)·7/2H <sub>2</sub> O	20	373.7	367.6		
Ag(dipic)(terpy)·4H <sub>2</sub> O	21	373.6	367.6		
[Ag(dipicH)(terpy)](S <sub>2</sub> O <sub>8</sub> ) <sub>0.5</sub> ·2H <sub>2</sub> O	22	373.8	367.7		
[Ag(quinH)(terpy)](S <sub>2</sub> O <sub>8</sub> ) <sub>0.5</sub>	23	373.9	367.7		
[Ag(lutH)(terpy)](S <sub>2</sub> O <sub>8</sub> ) <sub>0.5</sub> ·H <sub>2</sub> O	24	373.8	367.8		
[Ag(isocinchH)(terpy)](S <sub>2</sub> O <sub>8</sub> ) <sub>0.5</sub>	25	374.0	368.1		
[Ag(pic)(terpy)](S <sub>2</sub> O <sub>8</sub> ) <sub>0.5</sub> ·2H <sub>2</sub> O	26	373.7	367.7		

<sup>a</sup> Ligand abbreviations are given in the Experimental Section. All binding energies are referenced to the carbon 1s line of graphite at 284.0 eV. The silver 3d<sub>3/2</sub> and 3d<sub>5/2</sub> binding energies were located with a precision of ±0.1 eV. For the paramagnetic silver(II) complexes, which sometimes exhibited asymmetric peaks, the binding energy was taken at half of the FWHM.

were assigned to vibrations associated with the lattice water. A magnetic moment of 1.94 BM at 298°K was determined by the Gouy technique.

(iii) **Bis(isoquinoline-1-carboxylato)silver(II)**. This new complex was prepared by the conventional peroxydisulfate oxidation (using (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) of hot (75°) mixed aqueous solutions of silver nitrate and isoquinoline-1-carboxylic acid. An immediate orange precipitate of Ag(isoquin-1-COO)<sub>2</sub> formed when the silver nitrate solution was mixed with the other reagents. The reaction mixture was stirred for a few minutes and filtered while hot, and the orange-brown complex was washed with distilled water and dried *in vacuo* over calcium chloride. *Anal.* Calcd for C<sub>20</sub>H<sub>12</sub>AgN<sub>2</sub>O<sub>4</sub>: C, 53.1; H, 2.7; N, 6.2. Found: C, 53.7; H, 3.1; N, 5.5. The magnetic moment of this complex, determined by the Faraday method, was 1.81 BM at 297°K.

**Handling Precautions.** All silver complexes prepared in this study were stored in amber glass bottles and kept in a refrigerator to minimize decomposition during their handling. These precautions were especially necessary for most of the silver(I) complexes which were light sensitive.

**Physical Measurements.** Infrared spectra were recorded as Nujol mulls on a Beckman IR-10 or IR-12 spectrophotometer. The X-ray photoelectron spectra were recorded using a Hewlett-Packard Model 5950A ESCA spectrometer. Monochromatic aluminum Kα<sub>1,2</sub> radiation (1486.6 eV) was used as the X-ray excitation source and the powdered samples were dispersed on a gold-plated copper surface. For the silver compounds, the 3d core was the preferred level for the determination of binding energies. Accordingly, the spin-orbit levels 3d<sub>3/2</sub> and 3d<sub>5/2</sub>, of approximate relative intensity 4:6, were the ones whose binding energies were measured. In all instances, the silver 3d and nitrogen 1s binding energies are referenced to the C 1s line of graphite at 284.0 eV.<sup>21-23</sup> In addition to serving as an internal reference check, intimate grinding of the sample with graphite appeared to

eliminate sample charging effects. This procedure involved recording the Ag 3d<sub>3/2</sub> and 3d<sub>5/2</sub> binding energies of the undiluted complex and then diluting the sample with increasing amounts of graphite (usually using 1:2, 1:1, and 2:1 proportions) until the binding energies achieved constant values (±0.1 eV). In many instances, this procedure indicated that the undiluted samples had not charged since dilution with graphite did not shift the binding energies. Since the values of the binding energies we finally accepted for each compound resulted from several sample preparations and in view of their striking internal consistency (see Results and Discussion), we feel that surface potential problems are not important under our experimental conditions. Furthermore, the data were collected over a period of several months and we observed no variation of measured binding energies with time.<sup>24</sup> Indeed, as mentioned above, we routinely used the C 1s binding energy of graphite to monitor the performance of the instrument.

Visual examination of the samples after irradiation revealed no evidence for radiation damage. This is particularly significant in view of the sensitivity of many of the silver(I) complexes to light.

**Analytical Procedures.** Carbon, hydrogen, and nitrogen analyses were performed by Dr. C. S. Yeh in the microanalytical laboratory of this department. Silver was determined volumetrically using ammonium thiocyanate as the titrant and ferric ammonium sulfate as indicator.<sup>25</sup>

## Results

Silver 3d<sub>3/2</sub> and 3d<sub>5/2</sub> binding energies for the silver(I) and silver(II) complexes are given in Table I. In all instances, these energies are referenced to the carbon 1s peak of graphite at 284.0 eV. In several instances, the silver 3d binding energies were slightly higher (by *ca.* 1 eV) for the undiluted samples and the peaks were significantly broader than those of the diluted samples. These effects are the usual consequence of sample charging. In the case of the silver(II) complex Ag(dipic)(phen)·7/2H<sub>2</sub>O, charging of the *undiluted* sample was so severe and the peaks were so broad that the binding energies could not be located; a satisfactory spectrum was readily obtained when the sample was diluted with graphite.

For the silver(I) complexes, charging was not very important and the spin-orbit components 3d<sub>3/2</sub> and 3d<sub>5/2</sub> afforded symmetric peaks with relatively low half-widths (FWHM less

(21) Although a value of 284.3 eV has been quoted for the C 1s binding energy of graphite,<sup>22</sup> we reproducibly obtained a binding energy of 284.0 eV on our instrument. Since we are only interested in the relative binding energies of the silver(I) and silver(II) complexes, such a difference is not important. Our reference to a C 1s value of 284.0 eV can readily be compared to measurements of others,<sup>6,23</sup> who have used a 285.0-eV standard either for the C 1s binding energy of the hydrocarbon contaminant invariably present in their samples or for C 1s binding energy of Scotch tape, by applying a correction of 1.0 eV.

(22) U. Gelius, P. F. Heden, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling, and K. Siegbahn, *Phys. Scr.*, **2**, 70 (1970).

(23) G. L. Leigh and W. Bremser, *J. Chem. Soc., Dalton Trans.*, 1261 (1972).

(24) We thank a referee for drawing our attention to this point.

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

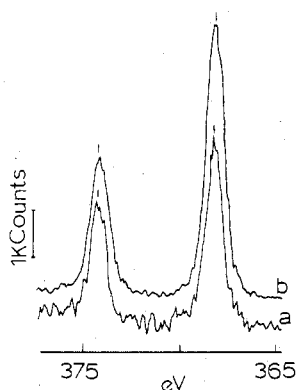


Figure 1. Silver  $3d_{3/2}$  and  $3d_{5/2}$  binding energies of the silver(I) complexes  $\text{Ag}(\text{phen})_2\text{NO}_3 \cdot \text{H}_2\text{O}$  (a) and  $\text{Ag}(\text{pyzCOO})$  (b).

than 1.2 eV).<sup>26</sup> Representative spectra are shown in Figure 1.

With few exceptions, the  $3d_{3/2}$  and  $3d_{5/2}$  peaks of the silver(II) complexes were significantly broader than those of the silver(I) derivatives and in several instances showed a marked asymmetry. These observations will be discussed further in the next section. Representative spectra are shown in Figure 2.

One additional point of note concerning differences between the 3d spectra of the silver(I) and silver(II) complexes was the much greater intensity of the 3d peaks of the former derivatives. This is in part probably due to the higher proportions of silver present in most of the silver(I) species.

In those instances where two types of nitrogen atom were present in the complexes, the nitrogen 1s binding energies were recorded. These data are also presented in Table I. As expected,<sup>27,28</sup> there is a clear distinction between nitrogen 1s energies of the nitrate ion and the coordinated nitrogen atoms of the heterocyclic ligand molecules. In addition to the binding energies associated with the nitrogen atoms of the pyridinecarboxylate molecules (at  $\sim 399$  eV), we observed in the case of the low-pH product "Ag(pic)" (compound 3), a further binding energy at 406.0 eV, of very low intensity, characteristic of the nitrate ion.<sup>27,28</sup> On the other hand, no such binding energy was observed in the related spectra of the high-pH form (compound 4), although nitrate ion is known to be present from the reaction of this product with 2,2'-bipyridyl.

## Discussion

**Silver  $3d_{3/2,5/2}$  Binding Energies.** For the silver(I) complexes these binding energies are insensitive to the nature of the central metal environment and fall into the rather narrow energy ranges 374.1–374.5 eV ( $3d_{3/2}$ ) and 368.0–368.5 eV ( $3d_{5/2}$ ). Comparison of these data with those for the silver(II) complexes (Table I) shows that this technique does not provide a reliable means of distinguishing the silver(I) and silver(II) species discussed in the present report. This is further borne out by studies on the mixed silver(I)–silver(II) complex of pyrazine-2,3-dicarboxylic acid (compound 9),<sup>11</sup> in which we observe no band doubling due to the presence of two formally different oxidation states of silver. The symmetric peaks are characteristic of the major silver(I) component of this system. Therefore, these results together with our data on low oxidation state rhodium<sup>29</sup> and rhenium<sup>30,31</sup> complex-

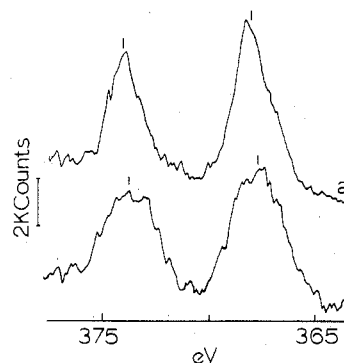


Figure 2. Silver  $3d_{3/2}$  and  $3d_{5/2}$  binding energies of the silver(II) complexes  $\text{Ag}(\text{pic})_2$  (a) and  $\text{Ag}(\text{dipic})(\text{terpy}) \cdot 4\text{H}_2\text{O}$  (b).

es indicate that for the *heavier transition elements in low oxidation states*, binding energy shifts are in most instances unlikely to provide a clear-cut assignment of the formal oxidation state. This is not surprising since small fractional changes in charge distribution at these relatively large metal centers (in covalent molecules) are unlikely to be reflected in very large binding energy shifts.

Within each series of silver(I) and silver(II) complexes, there is no significant shift of binding energies of cationic silver species relative to the neutral complexes—compare for example, compounds 10, 11, and 22 (Table I). This further illustrates the insensitivity of the silver 3d binding energies to changes in formal charge distribution.

One interesting and potentially useful trend is observed within the series of silver(II) complexes. The complex of pyridine-2,6-dicarboxylic acid,  $\text{Ag}(\text{dipic})(\text{dipicH}_2) \cdot 4\text{H}_2\text{O}$  (compound 18), which is known to contain a distorted six-coordinate stereochemistry,<sup>32,33</sup> has the lowest silver 3d binding energies, an observation which is consistent with the increase in coordination number relative to the planar complexes bis(picolinato)silver(II)<sup>19</sup> and bis(2,2'-bipyridyl)silver(II) peroxydisulfate.<sup>34,35</sup> This higher coordination number would result in an enhanced buildup of negative charge at the metal center with resulting decrease in metal electron binding energies. Furthermore, compounds 14, 19, 20, and 21 have binding energies intermediate between the low values for 18 and those of the planar complexes 10 and 11. For bis(pyridine-2,3-dicarboxylato)silver(II) dihydrate (14) this could be a reflection of the tetragonally distorted octahedral stereochemistry, established by a single-crystal X-ray analysis,<sup>1a</sup> and complexes 19, 20, and 21 almost certainly have five- or six-coordinate structures.<sup>1b</sup> However, while there is a marked tendency for the higher coordination numbers to exhibit lower binding energies, the total energy spread is sufficiently small that for silver(II) complexes this technique is unlikely to provide a clear-cut assignment of stereochemistry.

Little variation is found within the series of ionic complexes of the type  $[\text{Ag}(\text{pyridinecarboxylate})(\text{terpy})](\text{S}_2\text{O}_8)_{0.5} \cdot x\text{H}_2\text{O}$  suggesting that a similar stereochemistry (five- or six-coordinate) is present throughout the series of complexes 22–26.

(30) D. G. Tisley and R. A. Walton, *Inorg. Chem.*, **12**, 373 (1973).

(31) D. G. Tisley and R. A. Walton, unpublished work still in progress.

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

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

(34) The square-planar stereochemistry of the  $\text{Ag}(\text{bipy})_2^{2+}$  cation has been established from a single-crystal X-ray analysis of the salt  $\text{Ag}(\text{bipy})_2(\text{NO}_3)_2$ .<sup>35</sup>

(35) G. W. Bushnell and M. A. Khan, *Can. J. Chem.*, **50**, 315 (1972).

(26) FWHM = full width at half-maximum.

(27) D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, **8**, 2642 (1969).

(28) J. J. Jack and D. M. Hercules, *Anal. Chem.*, **43**, 729 (1971).

(29) A. D. Hamer, D. G. Tisley and R. A. Walton, *J. Chem. Soc., Dalton Trans.*, in press.

**Peak Widths.** As mentioned in the Results, many of the paramagnetic silver(II) species had  $3d_{3/2}$  and  $3d_{5/2}$  peaks which were markedly broader than those of the silver(I) complexes and in some instances distinctly asymmetric in contrast to the symmetric silver(I) peaks. This broadening effect may be due in part to "multiplet splittings" arising from coupling of the core 3d hole (essentially a "free ion" state) with the 4d valence shell ("crystal field" states). Previous work on simple oxides and fluorides of the first transition series and the lanthanides has revealed distinct splittings of the  $ns$  binding energies due to the various multiplet states formed by coupling a hole in the metal atom core to an unfilled valence shell.<sup>36,37</sup> Although theory is less straightforward for  $np$  binding energies, similar splittings,<sup>37</sup> or at least broadening effects,<sup>37,38</sup> can be attributed to multiplet splittings.

For the eight silver(I) species listed in Table I, the FWHM values for the silver  $3d_{3/2}$  and  $3d_{5/2}$  binding energies were  $1.1 \pm 0.1$  eV. On the other hand, with the exception of compounds **18** and **23**, the silver(II) complexes had an average FWHM value for these 3d binding energies of 2.4 eV, with a standard deviation of  $\pm 0.5$  eV. The  $3d_{3/2}$  and  $3d_{5/2}$  peaks of Ag(dipic)(dipicH<sub>2</sub>)·4H<sub>2</sub>O (**18**) and [Ag(quinH)(terpy)](S<sub>2</sub>O<sub>8</sub>)<sub>0.5</sub> (**23**) were relatively narrow and had FWHM values slightly greater than those of the silver(I) species: **18**  $3d_{3/2}$  1.3 eV,  $3d_{5/2}$  1.5 eV; **23**  $3d_{3/2}$  1.5 eV,  $3d_{5/2}$  1.6 eV. Also, although the two peaks of the spectrum of **23** were asymmetric, this was not the case for the spectrum of **18** which resembled closely the spectra of the silver(I) complexes. What seems likely is that broadening effects for these paramagnetic species, as typified by the multiplet splittings, will depend in part upon the detailed stereochemistry of the metal ions which will determine the relative orderings of the valence 4d orbitals. This in turn will affect the nature of possible multiplet states. Indeed, some preliminary theoretical calculations by Professor J. W. Richardson of this department have indicated that the change from a "free ion" Ag(II) species to one in an octahedral ligand field environment is accompanied by a significant increase in the energy spread of the multiplet

(36) R. L. Cohen, G. K. Wertheim, A. Rosencwaig, and H. J. Guggenheim, *Phys. Rev. B*, **5**, 1037 (1972).

(37) C. S. Fadley and D. A. Shirley, *Phys. Rev. A*, **2**, 1109 (1970).

(38) D. T. Clark and D. B. Adams, *Chem. Phys. Lett.*, **10**, 121 (1971).

states comprising the 3d binding energies. Accordingly it seems likely, particularly for the heavier transition elements in which the ligand field perturbations are rather large, that variations in stereochemistry will affect the observed peak widths.<sup>39</sup> Furthermore, at this stage it is not clear as to what effect these changes in stereochemistry will have upon the peak shapes. The apparent absence of radiation damage for the silver(I) and silver(II) complexes and the lack of variation of peak shapes both with the time of irradiation and with the history of the complexes (*i.e.*, the time between their preparation and spectral characterization) rule out the possibility that surface contaminants are contributing significantly to the observed spectra.

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**Registry No.** Ag(bipy)<sub>2</sub>NO<sub>3</sub>·2H<sub>2</sub>O, 33971-93-6; Ag(phen)<sub>2</sub>NO<sub>3</sub>·H<sub>2</sub>O, 16059-94-2; Ag<sub>2</sub>(dipic)·H<sub>2</sub>O, 12799-03-0; Ag(py<sub>2</sub>-COO), 33135-90-9; Ag<sub>2</sub>(py<sub>2</sub>-2,3-(COO)<sub>2</sub>), 36904-19-5; Ag<sub>3</sub>(py<sub>2</sub>-2,3,5-(COO)<sub>3</sub>)·H<sub>2</sub>O, 12799-02-9; Ag<sup>I</sup><sub>2</sub>Ag<sup>II</sup>(py<sub>2</sub>-2,3-(COO)<sub>2</sub>)<sub>2</sub>, 12799-04-1; Ag(bipy)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>·H<sub>2</sub>O, 28226-64-4; Ag(pic)<sub>2</sub>, 14783-00-7; Ag(isonic)<sub>2</sub>·H<sub>2</sub>O, 32210-56-3; Ag(isoquin-1-COO)<sub>2</sub>, 36904-22-0; Ag(quinH)<sub>2</sub>·2H<sub>2</sub>O, 36900-75-1; Ag(isocinchH)<sub>2</sub>, 19504-54-2; Ag(lutH)<sub>2</sub>·2H<sub>2</sub>O, 36926-56-4; Ag(cinchH)<sub>2</sub>·H<sub>2</sub>O, 12799-05-2; Ag(dipic)(dipicH<sub>2</sub>)·4H<sub>2</sub>O, 36900-76-2; Ag(dipic)(bipy)·3H<sub>2</sub>O, 12799-06-3; Ag(dipic)(phen)· $\frac{1}{2}$ H<sub>2</sub>O, 12799-07-4; Ag(dipic)(terpy)·4H<sub>2</sub>O, 12799-09-6; [Ag(dipicH)(terpy)](S<sub>2</sub>O<sub>8</sub>)<sub>0.5</sub>, 12799-10-9; [Ag(quinH)(terpy)](S<sub>2</sub>O<sub>8</sub>)<sub>0.5</sub>, 12799-11-0; [Ag(lutH)(terpy)](S<sub>2</sub>O<sub>8</sub>)<sub>0.5</sub>, 12799-12-1; [Ag(isocinchH)(terpy)](S<sub>2</sub>O<sub>8</sub>)<sub>0.5</sub>, 12799-13-2; [Ag(pic)(terpy)](S<sub>2</sub>O<sub>8</sub>)<sub>0.5</sub>, 12799-08-5.

(39) At present, the lack of definitive information on the magnitude of  $10Dq$  and of the relative orderings of the 4d orbitals for silver(II) complexes in a wide variety of stereochemistries precludes extensive calculations on the dependence of these peak widths upon the stereochemistry.