Cary 16 spectrometer fitted with a water-jacketed cell holder using 1-cm quartz cells. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz., and Dr. F. Pascher, Bonn, Germany.

Five-Coordinated Substituted Phenylacetyliridium(III) Complexes (1).—To a suspension of 300 mg of chlorodinitrogenbis(triphenylphosphine)iridium(I) in 3 ml of benzene was added 0.5 ml (or 0.5 g) of the acyl halide. There was vigorous nitrogen evolution and a deep red solution formed. Within 3 min, the complexes 1 precipitated as fibrous, orange solids. The pentafluorophenyl complex was precipitated from the red solution by slow addition of ether. The products were washed with small amounts of cool benzene followed by about 20 ml of ether. The solids were then dried for at least 24 hr *in vacuo* and stored under nitrogen (yield about 80–90%). Infrared spectra showed the products thus obtained contained very little or none of the six-coordinated carbonyl complexes 2. Molecular weights were determined in benzene solution. The preparation of the unsubstituted phenyl complex was as previously described.[7]

***cis*-Dichloro(substituted benzyl)bis(triphenylphosphine)carbonyliridium(III).**—To a suspension of 300 mg of the dinitrogen complex in 4 ml of benzene was added 0.5 ml (or 500 mg) of the acyl halide and the resulting orange mixture was stirred for 24 hr at room temperature. In the case of the pentafluorophenyl complex it was necessary to reflux the orange mixture for 2 hr. Filtration gave the colorless products (about 90% yield) which were recrystallized from benzene–*n*-hexane.

Kinetic Studies.—The reactions of the five-coordinate acyl complexes were followed by monitoring the decay of the absorption band at 480 nm for all the compounds. Plots of ln $(A - A_\infty)$ *vs.* time were linear with correlation coefficients in the range −0.997 to −0.999. The rate constants in Table III are in each case the average of three or four separate determinations. Temperatures were held constant within ±0.05°. Exposure of the reaction solutions to air was found to have no effect on the results. Changes in concentration of the acyl complex in the range 4–12 mg/10 ml of solvent had no effect on the rate constant. Kinetic runs for the phenylacetyl complex in the presence of an excess of phenylacetyl chloride (50:1 phenylacetyl chloride to complex) or of an excess of triphenylphosphine (20:1 $P(CrH_5)_3$ to complex) also gave linear ln $(A - A_\infty)$ *vs.* time plots.

Acknowledgment.—We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. This research was also supported by the National Science Foundation through the Grant GY 6152 College Science Improvement Program and Grant GY 7269.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
UNIVERSITY OF READING, READING, UNITED KINGDOM, AND PURDUE UNIVERSITY, LAFAYETTE, INDIANA 47907

Studies on Coordination Compounds of Silver(II). V.[1] The Preparation and Characterization of New Pyrazine and Pyrazine Carboxylate Complexes and Some Related Silver (I), Copper(II), Cobalt(II), and Nickel(II) Derivatives

BY R. W. MATTHEWS[2] AND R. A. WALTON*[3]

Received September 28, 1970

Pyrazine and several pyrazine carboxylic acids have been found to stabilize silver(II). Whereas bis(pyrazine-2-carboxylato)silver(II) is magnetically dilute and isostructural with square-planar bis(pyridine-2-carboxylato)silver(II), the pyrazine complex $[Ag(pyz)_2]S_2O_8$ contains polymeric square-planar cations and has magnetic properties (300–80°K) which can be interpreted in terms of an antiferromagnetic exchange interaction. Pyrazine-2,3-dicarboxylic acid forms an unusual silver complex which contains both silver(I) and silver(II) species. It is formulated as $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$ with an Ag(I):Ag(II) ratio of 2:1. The versatile complexing properties of this ligand are demonstrated by the preparation and structural elucidation of the related cobalt(II), nickel(II), copper(II), and silver(I) derivatives. Related studies on the silver(II)–pyrazine-2,3,5-tricarboxylic acid system are also described.

Introduction

From our studies on pyridine carboxylates of silver(II),[1,4–6] we established the stereochemistry of these derivatives in the hope of better understanding this relatively rare oxidation state and enabling a meaningful comparison to be made with the more common and stable copper(II) species. This oxidation state is usually unstable with respect to reduction to silver(I), and, indeed, silver(II) compounds can be important oxidants in organic chemistry. Also silver(II) species have been postulated as intermediates in kinetic studies involving silver(I)-catalyzed oxidations.[7]

Although most silver(II) complexes which are known are essentially insoluble in polar and nonpolar solvents, a fact which aides their isolation, some solubility in aqueous media is sometimes observed although such solutions are only stable for short periods of time. Thus the partial solubilities of silver(II) bis(pyridine-2,6-dicarboxylate) monohydrate and silver(II) bis(pyridine-2,3-dicarboxylate) dihydrate in water enabled us to isolate single crystals of these compounds. X-Ray analyses have now been completed[1,5,6] and provide a basis for interpreting the properties of other derivatives of silver(II).

Since pyrazine[8] and the pyrazinecarboxylic acids

---

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

[2] University of Reading.

[3] Address correspondence to this author at the Department of Chemistry, Purdue University, Lafayette, Ind. 47907.

[4] Part I: G. W. A. Fowles, R. W. Matthews, and R. A. Walton, *J. Chem. Soc. A*, 1108 (1968).

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

[6] Part III: M. G. B. Drew, R. W. Matthews, and R. A. Walton, *Inorg. Nucl. Chem. Lett.*, **6**, 277 (1970).

[7] See for example D. H. Huchital, N. Sutin, and B. Warnquist, *Inorg. Chem.*, **6**, 838 (1967); J. B. Kirwin, P. J. Proll, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **60**, 119 (1964); W. C. E. Higginson, D. R. Rosseinsky, J. B. Stead, and A. G. Sykes, *Discuss. Faraday Soc.*, **29**, 53 (1960).

[8] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1235 (1962); 3156, 5042 (1963).

combine the coordinating features of the pyridinecarboxylic acids, plus the fact that the pyrazine moiety may act as bridge and thus aid the formation of polymeric insoluble derivatives, we have now studied the role these molecules play in stabilizing this oxidation state. The results of these studies are described.

Experimental Section

Physical Measurements.—These were carried out as described in part I of this series.[4]

Ligands.—Commercially available samples of pyrazine (Koch-Light) were used. A sample of pyrazine-2-carboxylic acid was generously supplied by the Wyandotte Chemical Corp. This acid was also obtained by the simultaneous decarboxylation and sublimation of pyrazine-2,3-dicarboxylic acid at 190–210° and 2.5–4 mm pressure according to the method of Hall and Spoerri.[9] *Anal.* Calcd for $C_5H_4N_2O_2$: C, 48.4; H, 3.3; N, 22.6. Found: C, 48.3; H, 3.2; N, 23.3.

Permanganate oxidation of quinoxaline using the method of Jones and McLaughlin,[10] afforded pyrazine-2,3-dicarboxylic acid in satisfactory yield. *Anal.* Calcd for $C_6H_4N_2O_4$: C, 42.9; H, 2.4; N, 16.7. Found: C, 42.7; H, 2.4; N, 16.9.

Decarboxylation of pyrazine-2,3,5-tricarboxylic acid by prolonged boiling of an aqueous solution[11] gave pyrazine-2,6-dicarboxylic acid dihydrate in low yield (20% after recrystallization). *Anal.* Calcd for $C_6H_8N_2O_6$: C, 35.3; H, 4.0; N, 13.7. Found: C, 35.4; H, 3.9; N, 14.0.

Pyrazine-2,3,5-tricarboxylic acid was most conveniently prepared by the method of Mager and Berends.[11] The crystalline acid was isolated in about 30% yield as the dihydrate. *Anal.* Calcd for $C_7H_8N_2O_8$: C, 33.9; H, 3.3; N, 11.3. Found: C, 34.4; H, 3.3; N, 11.6.

Preparation of Complexes. (i) **Bis(pyrazine)silver(II) Peroxodisulfate.**—Sodium peroxodisulfate (11.0 g) was dissolved in a minimum volume of water at 0–5° and the solution was filtered. Pyrazine (1.0 g) was dissolved in the magnetically stirred filtrate and, on the addition of a solution of silver nitrate (0.95 g) in a small volume of water at 0–5°, a white solid precipitated. After stirring the reaction mixture at 0–5° for *ca.* 24 hr, the color of the precipitate changed to a dark red-brown. The insoluble complex was then filtered off, washed with water, and dried *in vacuo* over calcium chloride at 0–5°. The complex, obtained in nearly quantitative yield (94%), was stored at this same temperature to prevent decomposition to a silver(I) complex. *Anal.* Calcd for $C_8H_8AgN_4O_8S_2$: C, 20.9; H, 1.8; Ag, 23.4; N, 12.2. Found: C, 20.3; H, 1.7; Ag, 23.3; N, 12.0. The infrared spectrum of this complex (Nujol mull) in the 1350–400-cm^{-1} region was as follows (band assignments for ionic $S_2O_8^{2-}$ are given in parentheses;[12] the remaining bands are assigned to pyrazine): 1294 (s, br), ~1280 (sh) and 1240 (s, b) ($S_2O_8^{2-}$); 1221 (m); 1163 (ms); 1121 (s); ~1096 (w, doublet); 1056 (ms) ($S_2O_8^{2-}$); 1043 (s); 974 (w); ~855 (w, b); 820 (m); 801 (m); 690 and 680 (s, br) ($S_2O_8^{2-}$); 584 (s) ($S_2O_8^{2-}$); 562 and 557 (s) ($S_2O_8^{2-}$); 470 (s); 436 (w).

(ii) **Bis(pyrazine-2-carboxylato)silver(II).**—Ground-up pyrazine-2-carboxylic acid (2.45 g) was added to a solution of ammonium peroxodisulfate (28 g) in water (52 ml) at 0–5°, followed quickly by silver nitrate (1.6 g) in a small volume of water. The white precipitate, which separated immediately from the continuously stirred reaction mixture, quickly darkened, finally becoming dark red after 5 hr. The slightly water-soluble product, obtained in *ca.* 85% yield, was filtered off, washed with water, dried *in vacuo* over calcium chloride at 0–5°, and stored at this temperature. *Anal.* Calcd for $C_{10}H_6AgN_4O_4$: C, 33.9; H, 1.7; Ag, 30.5; N, 15.8. Found: C, 33.4; H, 1.8; Ag, 30.0; N, 15.4. Samples stored at room-temperature became paler after a few days. The infrared spectrum of this complex was similar to that of the copper(II) complex described below and that of $Ni(pyzCOO)_2 \cdot 2H_2O$.[13] Very intense carboxylate absorptions at 1620 and 1334 cm^{-1} were characteristic of covalently bonded –COO groups.[14]

(iii) **Bis(pyrazine-2-carboxylato)copper(II).**—The blue crystalline complex separated on mixing solutions of the acid (3.5 g) in water (175 ml) at pH 6–7 and copper(II) acetate monohydrate (3.5 g) in water (70 ml). The complex was washed with water and dried *in vacuo* over calcium chloride (yield 68%). *Anal.* Calcd for $C_{10}H_6CuN_4O_4$: C, 38.8; H, 2.0; Cu, 20.5; N, 18.1. Found: C, 39.15; H, 2.3; Cu, 20.3; N, 18.3. Infrared-active ν(COO) absorptions[14] were observed as very intense bands at 1634 and 1355 cm^{-1}.

(iv) **Pyrazine-2-carboxylatosilver(I).**—The lemon yellow light-sensitive complex precipitated quantitatively on adding an aqueous solution of silver nitrate (0.34 g) to a neutralized aqueous solution of the acid (0.28 g). *Anal.* Calcd for $C_5H_3AgN_2O_2$: C, 26.0; H, 1.3; Ag, 46.7; N, 12.1. Found: C, 25.8; H, 1.8; Ag, 46.6; N, 11.9. The infrared spectrum (Nujol mull) of this complex was similar to that of the copper(II) and silver(II) derivatives with ν(COO) at 1610 and 1350 cm^{-1}.

(v) **A Silver(II) Complex of Pyrazine-2,3-dicarboxylic Acid.**—In a series of 21 reactions in which the conditions were varied by altering reactant concentrations, the method of adding the reactants to the reaction mixture, and the temperature and time of reaction, we were able to establish the existence of a mixed silver(I)–silver(II) complex of stoichiometry $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$. The formation of this complex is very sensitive to the reaction conditions used, and we found it difficult to predict when conditions would yield the desired product. Some typical procedures which produced products approximating to this stoichiometry are described below. Analytical data are given in Table I.

TABLE I

ANALYTICAL DATA FOR $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$

Reaction product[a]	% C	% H	% N	% Ag	Av oxidn state of Ag[b]
a	20.2	0.8	8.1	48.3	1.30
b	22.3	0.7	8.4	48.2	1.31
c	20.5	0.7	8.0	48.6	1.30
d	21.3	0.7	8.2	47.1	1.32
Calcd for $C_{12}H_4Ag_3N_4O_8$	22.0	0.7	8.55	49.4	1.33[c]

[a] Letters refer to procedures given in the text. [b] Calculated as 1 + (% Ag(II) found/% Ag found). [c] Calculated assuming a Ag(I):Ag(II) ratio of 2:1.

(a) Ground-up pyrazine-2,3-dicarboxylic acid (2.0 g) was added to a continuously stirred solution of ammonium peroxodisulfate (20 g) in water (25 ml), quickly followed by a solution of silver nitrate (2.0 g) in water (2 ml). The mole ratio of Ag to acid was 1:1. The initial white precipitate quickly darkened to yield a red-brown product after stirring for 1 hr at room temperature. The complex was filtered off, washed with water, and dried *in vacuo* over calcium chloride.

(b) The method was the same as for (a), but the acid was initially dissolved in water before adding to the reaction mixture, and a reaction time of 2.5 hr was used. The product was orange-brown.

(c) Again the general method of (a) was followed but an Ag:acid ratio of 2:1, a reaction time of 4 hr, and a reaction temperature of 0–5° produced a red-brown product.

(d) An orange-brown complex was obtained by repeating (c) with a reaction time of 25 hr.

All told, 12 of the reactions we studied yielded this complex. The ratio of nitrogen to carbon in *all* the products obtained was in the range 1:2.92–1:3.03, indicating that the ligand remains intact in spite of the strong oxidizing conditions used in the reactions.

The infrared spectrum of this complex (Nujol mull) in the region 1700–400 cm^{-1} is as follows (Nujol bands omitted): 1628 (s), 1565 (vs), 1375 (m) (coincident with the Nujol band), 1335 (s), 1217 (m), 1192 (vw), 1175 (ms), 1121 (s), 1069 (m), 984 (vw), 892 (ms), 881 (m), 836 and 833 (s), 780 (m), 741 (ms), 730 (m), 691 (m), 614 (w), 558 (m), 472 (ms), 455 (s).

(vi) **Pyrazine-2,3-dicarboxylatocopper(II).**—The green 1:1 complex was precipitated in 82% yield on mixing aqueous solutions of neutralized acid and excess cupric acetate monohydrate. *Anal.* Calcd for $C_6H_2CuN_2O_4$: C, 31.4; H, 0.9; Cu, 27.7; N, 12.2. Found: C, 31.0; H, 1.0; Cu, 28.0; N, 12.0. The infrared spectrum of this complex (Nujol mull) in the region 1700–400 cm^{-1} is as follows (Nujol bands omitted): ~1690 (sh), ~1654 (vs, b), 1580 (s), 1425 (m), 1325 (vs, b), ~1245 (sh),

---

(9) S. A. Hall and P. E. Spoerri, *J. Amer. Chem. Soc.*, **62**, 664 (1940).

(10) R. G. Jones and K. C. McLaughlin, *Org. Syn.*, **30**, 86 (1950).

(11) H. I. X. Mager and W. Berends, *Recl. Trav. Chim. Pays-Bas*, **77**, 827 (1958).

(12) H. Richter, *Z. Anorg. Allg. Chem.*, **315**, 196 (1962).

(13) R. W. Matthews, unpublished observations.

(14) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 5262 (1962).

1219 (vw), 1197 (m), 1176 (ms), 1129 (s), 1081 (m), 1057 (w), 912 (w), 893 (ms), 873 (w), 852 (ms), 841 (mw), 784 (m), 769 (mw), 742 (w), 725 (mw), 671 (mw), 611 (w), 545 (ms), 501 (ms), 488 (m), 455 (w), 442 (m), 423 (mw).

(vii) **Bis(pyrazine-2,3-dicarboxylato)cobalt(II) Dihydrate.**—A solution of the acid (3.36 g) in 60 ml of water was added to 2.4 g of cobalt(II) nitrate hexahydrate. The resulting solution was maintained at 0–5° for 24 hr. The resulting orange crystals were filtered off, washed with water, and dried *in vacuo* (yield 90%). *Anal.* Calcd for $C_{12}H_{10}CoN_4O_{10}$: C, 33.6; H, 2.4; Co, 13.7; N, 13.1. Found: C, 32.8; H, 2.4; Co, 14.2; N, 12.9. A thermogravimetric analysis of this complex showed that it decomposed continuously between 200 and 500° to leave Co_3O_4 (wt loss: calcd, 81.3%; found, 80.9%).

(viii) **Bis(pyrazine-2,3-dicarboxylato)nickel(II) Dihydrate.**—A similar procedure to that described for (vii) gave an 80% yield of green complex. *Anal.* Calcd for $C_{12}H_{10}NiN_4O_{10}$: C, 33.6; H, 2.4; Ni, 13.7; N, 13.1. Found: C, 33.9; H, 2.4; Ni, 13.7; N, 13.4. A tga analysis was similar to that of the cobalt complex, with decomposition over the temperature range 140–550° to leave NiO (wt loss: calcd, 82.6%; found, 81.9%). The infrared spectra of the cobalt(II) and nickel(II) complexes were virtually identical. Absorption band frequencies in the spectrum of the nickel complex are as follows (Nujol bands omitted): 3435 (s) and 3320 (ms) (ν(O–H)), 1686 (ms), 1615 (m, b), 1540 (s, b), 1240 (m, b), 1212 (mw), ~1160 (sh), 1110 (s), 1060 (mw), 880 and 874 (m), 840 (mw), 764 (ms), 682 (mw), 660 (m), ~610 (w), 513 (m), 482 (m), 443 (m), ~412 (w).

(ix) **Pyrazine-2,3-dicarboxylatosilver(I).**—The pale yellow light-sensitive complex $Ag_2(C_6H_2N_2O_4)$ precipitated on mixing aqueous solutions of excess silver nitrate and neutralized pyrazine-2,3-dicarboxylic acid. The product, obtained in 84% yield, was filtered off, washed with warm water, and dried *in vacuo* over calcium chloride. *Anal.* Calcd for $C_6H_2AgN_2O_4$: C, 18.9; H, 0.5; Ag, 56.5; N, 7.3. Found: C, 18.5; H, 0.7; Ag, 55.9; N, 7.3. Infrared absorption bands in the 1700–1350-cm^{-1} region are as follows (Nujol bands omitted): 1610 (sh), 1590 (s), 1560 (m), ~1540 (sh), 1421 (w), 1380 (s).

(x) **The Attempted Isolation of a Silver(II) Complex with Pyrazine-2,3,5-tricarboxylic Acid.**—Investigations under various conditions of the peroxodisulfate oxidation of silver(I) to silver(II), in the presence of this acid, failed to yield a stoichiometric product. It is worthwhile, however, to comment on the general features of the products of these reactions.

On treating 2 mol or more of silver nitrate with 1 mol of acid in peroxodisulfate solution at room temperature, the initial pale yellow precipitate was converted to a dark brown solid after *ca.* 10 min. Analysis of the products collected after 10–40 min revealed little destruction of the ligand (C:N = 7:2) but longer reaction times resulted in effervescence of the reaction mixture and evolution of CO_2 with the C:N ratios now appreciably below 7:2. The products liberated iodine from aqueous potassium iodide and, when obtained from the shorter timed reactions, they had total silver to silver(II) ratios of 2.64:1 to 3.18:1. Some representative analytical data for short reaction time products are as follows. Found (for three separate runs): total Ag, 50.0, 50.7, 49.7; Ag(II), 15.75, 16.95, 18.7; C, 18.9, 18.5, 19.1; H, 0.3, 0.4, 0.45; N, 6.1, 6.2, 6.5.

These products exhibited electronic spectra characteristic of square-planar silver(II) species,[4] with the lowest energy band located at ~19,500 cm^{-1} (sh) in the diffuse-reflectance spectrum, were paramagnetic,[15] and became paler when stored at room temperature for a few days. Infrared absorption bands in the 1700–1250-cm^{-1} region are as follows (Nujol bands omitted): 1625 (vs, b), 1414 (w), 1345 (mw), 1305 (sh), 1293 (ms).

(xi) **Bis(pyrazine-2,3,5-tricarboxylato)tricopper(II) Heptahydrate.**—The pale green complex precipitated in 90% yield when aqueous solutions of the acid (2 mol) and copper(II) acetate monohydrate (3.3 mol) were mixed. It was washed with water, ethanol, and ether and then air dried. *Anal.* Calcd for $C_{14}H_{16}Cu_3N_4O_{19}$: C, 22.9; H, 2.2; Cu, 25.9; N, 7.6. Found: C, 23.3; H, 1.9; Cu, 25.4; N, 7.5. A very intense infrared absorption band centered at ~3390 cm^{-1} is assigned to ν(O–H). In the region characteristic of –COO vibrations (1700–1250 cm^{-1}), the following bands were observed (Nujol bands omitted): 1652 (vs, vb), 1432 (ms), 1363 (ms), 1318 (s).

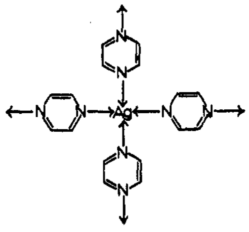
(xii) **(Pyrazine-2,3,5-tricarboxylato)trisilver(I) Monohydrate.**—This pale yellow, light-sensitive complex was prepared in 70% yield by a method analogous to that employed for (ix). *Anal.* Calcd for $C_7H_3Ag_3N_2O_7$: C, 15.3; H, 0.6; Ag, 58.8; N, 5.1. Found: C, 14.9; H, 0.5; Ag, 57.7; N, 4.8. Relevant infrared absorption bands are as follows (Nujol bands omitted): ~3350 (b) (ν(O–H)), 1590 (vs, vb), 1365 (m), 1312 (s).

Analytical Procedures.—Total silver and silver(II) were determined as described previously.[4,16] Determination of copper was affected by interference from the ligand molecules. Consequently the organic matter was first destroyed either by repeated evaporation of the complex with concentrated nitric acid or by very slowly heating the complex, to yield, in both cases, CuO. The oxide was dissolved in warm dilute H_2SO_4 and the copper was determined by the iodide–thiosulfate method. Nickel was determined gravimetrically using dimethylglyoxime and cobalt spectrophotometrically with R-nitroso salt in buffered solution.

Results and Discussion

The new silver(II) complexes of pyrazine $Ag(pyz)_2S_2O_8$ and pyrazine-2-carboxylic acid $Ag(pyzCOO)_2$ were prepared by conventional oxidation procedures[4] employing sodium or ammonium peroxodisulfates as oxidants.

By analogy with the pyridine complex $Ag(py)_4S_2O_8$,[17] the pyrazine derivative might be expected to involve a square-planar arrangement of nitrogen atoms around the silver (see I) with *bridging* pyrazine molecules.



I

Evidence for this possibility is obtained from infrared measurements (see Experimental Section). Stidham and Chandler[18] have suggested that the appearance of a *weak* pyrazine band in the 950–1000-cm^{-1} region indicates moderate polymer chain length with bridging pyrazine molecules. Thus $AgNO_3pyz$, which is known to contain bridging pyrazine molecules,[19] shows a medium weak band at 990 cm^{-1}. Our results for $Ag(pyz)_2S_2O_8$, for which we observe a *weak* band at 974 cm^{-1}, provides support for I.

The diffuse-reflectance spectrum (Table II and Figure 1) of $Ag(pyz)_2S_2O_8$ shows its lowest energy band at 19,000 cm^{-1}, consistent with an essentially square-planar stereochemistry.[4,5] The magnetic moment at room temperature (1.61 BM) is less than the spin-only value and its marked temperature dependence (Table III) is not characteristic of the magnetic behavior of magnetically dilute square-planar or octahedral silver(II) species.[4] The magnetic susceptibility obeys the Curie–Weiss law with a Weiss constant of 84°K, is reminiscent of the previously reported[4] magnetic behavior of silver(II) nicotinate, and indicates the presence of a significant antiferromagnetic exchange interaction. In the absence of a single-crystal X-ray anal-

---

[15] For the product analyzing as follows, the magnetic moment was observed to be ~1.6 BM per silver(II): total Ag, 49.7; Ag(II), 18.7; C, 19.1; H, 0.45; N, 6.5.

[16] See the Ph.D. thesis of R. W. Matthews, University of Reading, 1969, for full details.

[17] J. A. McMillan, *Chem. Rev.*, **62**, 65 (1962).

[18] H. D. Stidham and J. A. Chandler, *J. Inorg. Nucl. Chem.*, **27**, 397 (1965).

[19] R. G. Vranka and E. L. Amma, *Inorg. Chem.*, **5**, 1020 (1966).

TABLE II

DIFFUSE-REFLECTANCE SPECTRA OF COMPLEXES OF PYRAZINE AND THE PYRAZINECARBOXYLIC ACIDS

Compound	Absorption max, cm^{-1} $d \leftrightarrow d$	 Charge transfer
$Ag(pyz)_2S_2O_8$[a]	19,000	25,800, 32,700, 37,400
$Ag(pyzCOO)_2$[b]	20,600	29,600, 37,400
$Cu(pyzCOO)_2$[b]	16,500	24,600, 31,600, 37,800
$Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$[b]	~25,000	28,700, 36,900
$Cu(C_6H_2N_2O_4)$[b]	16,000	~24,000 sh, 30,400, 37,000
$Co(C_6H_3N_2O_4)_2 \cdot 2H_2O$[b]	9,200 21,000 sh	30,100, 37,600
$Ni(C_6H_3N_2O_4)_2 \cdot 2H_2O$[b]	10,400 11,800 16,800 26,200	31,200, 37,600
$Cu_3(C_7HN_2O_6)_2 \cdot 7H_2O$[b]	13,600	~25,000 sh, 32,000, 36,600

[a] LiF used as reference. [b] MgO used as reference.

ysis on this complex no information is yet available on the mechanism of this magnetic exchange.

The silver(II) and copper(II) (μ_{eff} = 1.81 BM at 295°) complexes of pyrazine-2-carboxylic acid have normal magnetic behavior (Table III) and diffuse-reflectance spectra (Table II and Figure 1) characteristic of square-planar metal species with bands at 20,000 and 16,500 cm^{-1}, respectively, assigned to metal ion $d \leftrightarrow d$ transitions. The values of the room-temperature magnetic moments of these complexes and the lack of temperature variation of the moment of the silver(II) complex (Θ = +8°K) suggest that these are magnetically dilute square-planar species. These two complexes almost certainly have closely related structures to those of silver(II) and copper(II) picolinates.[4,20]

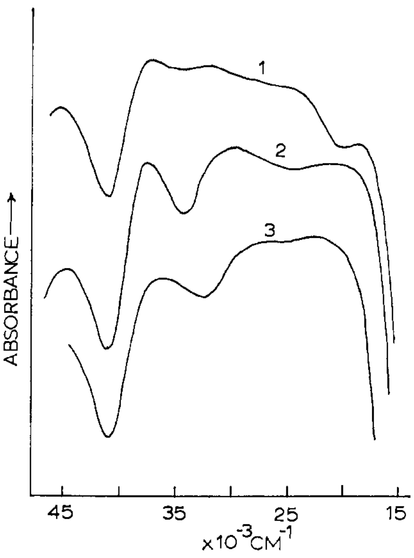
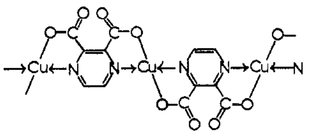


Figure 1.—The diffuse-reflectance spectra of (1) $Ag(pyz)_2S_2O_8$, (2) $Ag(pyzCOO)_2$, and (3) $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$.

However, the stabilities of bis(pyridine-2-carboxylato)silver(II) and bis(pyrazine-2-carboxylato)silver(II) are markedly different. Whereas the former is stable for months at room temperature, the pyrazine-2-carboxylate can only be successfully prepared at 0–5° and on storing at room temperature for a few days it decomposes to the yellow silver(II) complex. The decreasing stability observed on passing from the pyridine- to the pyrazine-based complex is also found on comparing $Ag(py)_4S_2O_8$ with $Ag(pyz)_2S_2O_8$. The pyridine complex is stable at room temperature[21] but successful preparation of the pyrazine complex requires a temperature near 0°.

Perhaps the most surprising result in the present study was our isolation of the red-brown mixed silver(I)–silver(II) complex of pyrazine-2,3-dicarboxylic acid $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$. We had first anticipated that we would isolate a complex analogous to the copper(II) derivative $Cu(C_6H_2N_2O_4)$ which we believe most likely has the polymeric structure of II, since its diffuse-reflectance spectrum (Table II) and magnetic data (Table III) indicate an essentially square-planar coordination around Cu, and the infrared spectral data and insolubility in water support a polymeric structure.



II

The evidence that we have correctly formulated the mixed-silver complex is as follows. First, oxidation-state titrations (Table I) reveal a total silver to silver(II) ratio of 3:1. Second, the diffuse-reflectance spectra (Table II and Figure 1) exhibit a broad lowest energy band in the region 22,000–25,000 cm^{-1}, similar to that found for most pyridinecarboxylate complexes of silver(II).[4] Third, the products are paramagnetic, with magnetic moments at room temperature of 1.76 and 1.71 BM for two separate preparations. The moment of the first sample was also determined over a temperature range and found to be essentially independent of temperature with Θ = +2°K (Table III). Finally, the infrared spectrum of this complex showed the absence of free –COOH groups, both carboxyl groups being bonded.

The possibility that this complex was a mixture of the silver(I) complex $Ag_2(C_6H_2N_2O_4)$ (see below) and a silver(II) complex $Ag(C_6H_2N_2O_4)$, similar to the copper(II) complex, was investigated from X-ray powder measurements. As shown in Table IV the interplanar spacings of the authentic silver(I) complex, particularly at low 2Θ values, are not repeated in the pattern of $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$. While this is good evidence for the existence of a discrete Ag(I)–Ag(II) complex rather than a mixture, the possibility cannot be ruled out that the silver(I) complex could crystallize in different space groups under the different conditions used to prepare $Ag_2(C_6H_2N_2O_4)$ and the Ag(I)–Ag(II) complex.[22]

A further consideration of the infrared spectra of the free acid, $Cu^{II}(C_6H_2N_2O_4)$, $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$, and the silver(I) complex $Ag^{I}_2(C_6H_2N_2O_4)$ gives a clue as to the structures of the silver complexes (see Experimental Section and Figure 2). The band structure centered at ~1700 cm^{-1} and the broad band at ~1260 cm^{-1} in the mull spectrum of the free acid are readily assigned to C–O bond stretching vibrations of the COOH group. In the copper(II) complex, the related vibrations are centered at ~1645 and 1325 cm^{-1}, respectively, as ex-

---

(20) (a) E. G. Cox, W. Wardlaw, and K. C. Webster, *J. Chem. Soc.*, 775 (1936); (b) E. C. Lingafelter and H. J. Clegg, Abstracts, American Crystallographic Association Winter Meeting, New Orleans, La., 1970, No. C1, p 25.

(21) G. A. Barbieri, *Gazz. Chim. Ital.*, **42**, 7 (1912).

(22) We thank a referee for suggesting this possibility.

TABLE III

TEMPERATURE DEPENDENCE OF THE MAGNETIC PROPERTIES OF THE SILVER(II), COPPER(II), COBALT(II), AND NICKEL(II) COMPLEXES[a]

$Ag(pyz)_2S_2O_8$	T[b]	299	289	281	273	263	233	203
(θ = +84°)	$10^6\chi'_m$[c]	1076	1101	1126	1147	1184	1303	1450
	μ_{eff}[d]	1.61	1.60	1.60	1.59	1.59	1.57	1.54
	T	173	143	123	109	95	83	
	$10^6\chi'_m$	1624	1837	1999	2133	2269	2421	
	μ_{eff}	1.51	1.46	1.41	1.37	1.32	1.27	
$Ag(pyzCOO)_2$	T	299	291	283	273	263	233	203
(θ = +8°)	$10^6\chi'_m$	1325	1362	1397	1456	1509	1694	1946
	μ_{eff}	1.79	1.79	1.79	1.79	1.79	1.78	1.79
	T	173	143	113	85			
	$10^6\chi'_m$	2269	2718	3360	4374			
	μ_{eff}	1.78	1.77	1.75	1.73			
$Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$	T	299	291	283	273	263	233	203
(θ = +2°)	$10^6\chi'_m$	1285	1321	1368	1416	1472	1664	1912
	μ_{eff}	1.76	1.76	1.77	1.77	1.77	1.77	1.77
	T	173	143	113	95			
	$10^6\chi'_m$	2252	2710	3384	3973			
	μ_{eff}	1.77	1.77	1.76	1.74			
$Cu(C_6H_2N_2O_4)$	T	303	297	287	275	263	233	203
(θ = +4°)	$10^6\chi'_m$	1384	1412	1459	1523	1592	1802	2065
	μ_{eff}	1.84	1.84	1.84	1.84	1.84	1.84	1.84
	T	173	143	113	89			
	$10^6\chi'_m$	2414	2897	3605	4496			
	μ_{eff}	1.84	1.83	1.81	1.80			
$Cu_3(C_7HN_2O_6)\cdot 7H_2O$	T	299	289	281	273	263	233	203
(θ = +14°)	$10^6\chi'_m$	1366	1408	1460	1490	1550	1731	1984
	μ_{eff}	1.82	1.81	1.82	1.81	1.81	1.80	1.80
	T	173	143	113	89			
	$10^6\chi'_m$	2330	2742	3376	4162			
	μ_{eff}	1.80	1.78	1.76	1.73			
$Co(C_6H_3N_2O_4)_2\cdot 2H_2O$	T	299	289	281	273	263	233	203
(θ = +15°)	$10^6\chi'_m$	9402	9663	9931	10,214	10,572	11,848	13,515
	μ_{eff}	4.76	4.75	4.75	4.74	4.74	4.72	4.71
	T	173	143	113	91			
	$10^6\chi'_m$	15,690	18,685	23,066	27,871			
	μ_{eff}	4.68	4.65	4.59	4.53			
$Ni(C_6H_3N_2O_4)_2\cdot 2H_2O$	T	299	289	281	273	263	233	203
(θ = +12°)	$10^6\chi'_m$	4189	4309	4428	4564	4712	5308	6060
	μ_{eff}	3.18	3.17	3.17	3.17	3.16	3.16	3.15
	T	173	143	113	95			
	$10^6\chi'_m$	7086	8460	10,531	12,347			
	μ_{eff}	3.15	3.13	3.10	3.08			

[a] TIP not allowed for in the silver(II) complexes; for the copper(II) complexes a value of 60 × 10^{-6} cgsu was assumed. [b] Temperature in degrees Kelvin. [c] In cgs units. [d] Bohr magnetons.

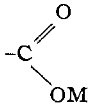
TABLE IV

X-RAY POWDER DATA FOR $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$ AND $Ag_2(C_6H_2N_2O_4)$[a]

$Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$				$Ag_2(C_6H_2N_2O_4)$			
I	d, Å	I	d, Å	I	d, Å	I	d, Å
37	11.68	69	3.16	5	9.21	5	3.22
100	5.86	32	3.00	56	6.48	44	2.99
45	5.72	13	2.94	100	5.45	67	2.79
39	4.89	5	2.74	4	4.72	5	2.65
55	3.99	9	2.64	22	4.03	22	2.61
13	3.87	12	2.61	13	3.85	25	2.51
29	3.78	11	2.59	5	3.66	31	2.48
19	3.59	15	2.50	15	3.44	4	2.39
7	3.48	17	2.48	69	3.31		
24	3.38	31	2.40				
28	3.31						

[a] I = relative intensity; d = interplanar spacing.

pected for a complex containing the



moiety.[14] On the other hand, for $Ag^{I}_2(C_6H_2N_2O_4)$ these bands are at ~1590 and 1380 cm^{-1}, frequencies which are close to those characteristic of the presence of bridging carboxylate groups.[14] Accordingly we suggest that the silver(I) complex has the polymeric structure

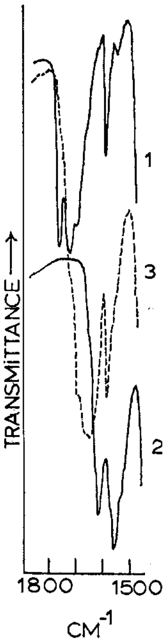
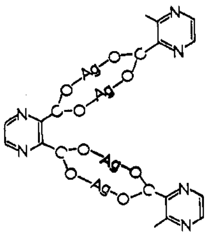


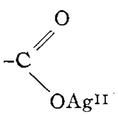
Figure 2.—Infrared spectra (Nujol mulls) of (1) pyrazine-2,3-dicarboxylic acid, (2) $Ag^{II}Ag^{I}_2(C_6H_2N_2O_4)_2$, and (3) $Cu(C_6H_2N_2O_4)$, in the region 1800–1500 cm^{-1}.

of III.

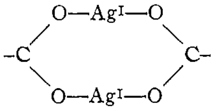


III

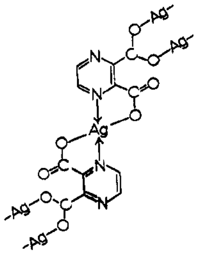
The spectrum of the mixed silver(I)–silver(II) complex shows characteristics of both types of metal–carboxylate bonding, with the bands at 1628 and 1335 cm^{-1} assigned to ν(C–O) of the moiety and those at 1565 and 1375 cm^{-1} to bridges of the type involving the silver(I) atoms.



$-C(=O)OAg^{II}$



Thus we suggest that this unique complex has the polymeric structure of IV, in which $Ag^{II}(C_6H_2N_2O_4)_2$ units are bridged by silver(I) atoms.

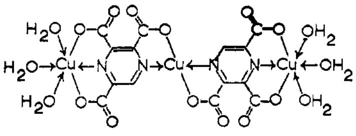


IV

The complexes of cobalt(II) and nickel(II) with pyrazine-2,3-dicarboxylic acid are of stoichiometry $M(C_6H_3N_2O_4)_2 \cdot 2H_2O$ and contain metal ions in pseudooctahedral environments. Their magnetic properties are normal for such a stereochemistry[23] (Table III), and their diffuse-reflectance spectra (Table II) may be assigned in the usual fashion,[24] assuming that the stereochemistry "approaches" octahedral: $Co(C_6H_3N_2O_4)_2 \cdot 2H_2O$, $\nu_1(^4T_{1g} \rightarrow {}^4T_{2g})$ 9200 cm^{-1}, $\nu_3(^4T_{1g} \rightarrow {}^4T_{1g}$ (P)) 21,000 cm^{-1} (sh), $Ni(C_6H_3N_2O_4)_2 \cdot 2H_2O$, $\nu_1(^3A_{2g} \rightarrow {}^3T_{2g})$ 10,400 and 11,800 cm^{-1} (doublet), $\nu_2(^3A_{2g} \rightarrow {}^3T_{1g}$ (F)) 16,800 cm^{-1}, and $\nu_3(^3A_{2g} \rightarrow {}^3T_{1g}$ (P)) 26,200 cm^{-1}. Their infrared spectra reveal the presence of covalently bonded carboxylate groups and "free" –COOH (*e.g.*, ν(C–O) at 1686 cm^{-1} for the nickel complex), so that each ligand molecule coordinates to a metal ion through the 1 nitrogen atom and an oxygen atom of the 2-carboxylate group. Whether the primary coordination sphere is completed by coordination from the two water molecules or by the carboxyl groups of the –COOH groups in the 3 positions of *adjacent* $M(C_6H_3N_2O_4)_2$ molecules (in a similar fashion to that observed in bis(pyridine-2,3-dicarboxylato)silver(II) dihydrate)[6] is uncertain.

Although silver(II) is stabilized in the pyrazine-2,3,5-tricarboxylic acid system, we were unable to develop a preparative procedure to yield reproducibly a stoichiometric product. Two likely reasons for the ineffectiveness of preparative procedures are (1) the ease with which the ligand decarboxylates under the reaction conditions (see Experimental Section) and (2) the instability of the silver(II) complex once formed.

In the infrared spectra of the copper(II) and silver(I) derivatives of this acid, the spectra are dominated by very intense broad absorptions centered at 1652 and 1590 cm^{-1}, respectively, similar to the frequency differences observed between ν(C–O) of the related pyrazine-2,3-dicarboxylates. Accordingly we suggest that $Ag_3(C_7HN_2O_6) \cdot H_2O$ has a polymeric structure related to that of IV. The copper(II) complex $Cu_3(C_7HN_2O_6)_2 \cdot 7H_2O$ is magnetically dilute (Table III) and the d $\leftrightarrow$ d transitions associated with this complex are contained in a very intense broad asymmetric absorption band centered at 13,600 cm^{-1}. In view of the above observations and the realization that this acid formally has the bonding characteristics of the pyridine-2- and -2,6-carboxylic acids, this derivative may have the structure of V and thus contain pseudooctahedral and square-planar copper(II) species, with a further molecule of water in the crystal lattice.



V

Acknowledgments.—We are grateful to the University of Reading for the award of a studentship to R. W. M. during the period 1966–1969. We thank Professor G. W. A. Fowles for his interest in this work. R. A. W. gratefully acknowledges support through a Purdue University Research Foundation XL grant.

---

(23) See B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964), and references therein.

(24) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, pp 256 and 261.