fluxed for 16 hr and then cooled to 25°. The precipitate was filtered off, washed with tetrahydrofuran, and dried (111.7 g). This material was then washed with water to remove triethylamine hydrochloride (78.9 g; theory, 82 g). The residue was crude IX (32.8 g, 72.3%). This material was recrystallized from aqueous acetone or methyl ethyl ketone to yield white or pale yellow needles of **tris(*o*-phenylenediamino)cyclotriphosphazene**. The compound did not melt below 300° and could not be sublimed at 300° (0.5 mm). It was insoluble in hexane, benzene, toluene, dioxane, carbon tetrachloride, and water. It was sparingly soluble in acetone, acetonitrile, or methyl ethyl ketone.

Analyses.—Analytical data for compounds IV to VII and IX are shown in Table I.

Polymerizations.—Polymerizations were attempted by heating samples of each compound under vacuum at temperatures up to 300° for between 4 and 8 hr. Any changes were followed by infrared spectra and melting point. The weight-average molecular weight value of the linear macrocyclic polymer produced from I (after removal of trimer at 300° (0.05 mm)) was found to be 13,000 by light-scattering measurements in dimethylformamide. The brittle polymer produced from IV after 5 hr at 300° under vacuum was too insoluble for the molecular weight to be determined. Infrared spectra suggested that rearrangement of both the phosphazene and naphthyldioxyphosphole units had occurred.

Acknowledgment.—We thank Dr. J. Lancaster and Mrs. M. Neglia for the nmr results and Mr. J. Koren, Dr. D. Maricle, and Dr. J. H. Deonarine for the ultraviolet, polarographic, and analytical data. We are indebted to Dr. L. A. Siegel for the X-ray crystallographic measurements.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTH CAROLINA, COLUMBIA, SOUTH CAROLINA 29208

Metal Ion–Aromatic Complexes. II. The Crystal Structure of the 1:1 Silver Nitrate–Pyrazine Complex

BY R. G. VRANKA[1] AND E. L. AMMA[2]

Received November 2, 1965

The crystal structure of the 1:1 silver nitrate–pyrazine complex has been determined by three-dimensional, single-crystal X-ray diffraction techniques. The structure consists of almost planar-kinked chains of the type $[-Ag-NC_4H_4N-]_x$ with Ag–N distances of 2.213 ± 0.014 A and N–Ag–N′ angles of 159.2 ± 0.9°. Next nearest neighbors of Ag(I) are two oxygens of a nitrate group at 2.720 ± 0.021 A and two other nitrate oxygens at 2.943 ± 0.017 A. The chains are held together by weak or van der Waals interactions. The crystals are all inherently twinned.

Introduction

Covalently bonded Ag(I) is most commonly found with a coordination number of two or four with linear and tetrahedral geometry, respectively. The best known examples with coordination number two are linear $Ag(NH_3)_2^+$ and $Ag(CN)_2^-$.[3a] An example of tetrahedral fourfold coordination is $Ag[SC(CH_3)NH_2]_4Cl$.[4] However, Ag(I) also forms crystalline organic complexes with completely different geometries and bonding from the above. Some of these are: $Ag^+\cdot C_6H_6\cdot ClO_4^-$,[5] $Ag^+\cdot C_8H_8\cdot NO_3^-$,[6] $Ag^+C_6H_6\cdot AlCl_4^-$,[7] and $Ag^+\cdot 3C_4H_8O_2\cdot ClO_4^-$.[8] The first three are "π" complexes, and the fourth is an "ionic" complex with octahedral coordination about Ag(I).

The complex $AgNO_3\cdot N_2C_4H_4$[9] recently was prepared, and some of its physical properties were reported. The complex was found to be stable in air and insoluble in water—unusual properties for this type of compound.

As part of a continuing structure study of metal ion–aromatic complexes, a crystal structural investigation of this compound was undertaken to determine the stereochemical reasons for its stability as well as to observe the effect of complex formation on the aromatic system.

Experimental Section

Needle crystals of $AgNO_3\cdot N_2C_4H_4$ appropriate for diffraction purposes were grown by the slow cooling of a reaction mixture of pyrazine and silver nitrate in warm water.[9] Precession and Weissenberg photographs taken with Mo Kα radiation revealed the crystals to be monoclinic with $a = 14.21 \pm 0.04$, $b = 6.47 \pm 0.02$, $c = 3.56 \pm 0.01$ A, and $\beta = 95° 15' \pm 10'$ (Mo Kα = 0.7107 A). The calculated density of 2.53 g cm^{-3}, based on two formula species per unit cell, is in satisfactory agreement with the experimental value of 2.56 g cm^{-3} obtained by the flotation method. Systematic absences of $h = 2n + 1$ for $h0l$ indicate the probable space group to be Pa or P2/a. The choice between the space groups was established by the X-ray analysis (*vide infra*). A needle crystal of 0.10 × 0.15 × 0.80 mm dimensions was mounted about the needle axis and used for collecting the intensity data. Since the linear absorption coefficient (μ) for this compound with Mo Kα radiation is only 34 cm^{-1}, no absorption corrections were made.

Equiinclination Weissenberg multiple-film intensity data were collected for $hk0$–$hk3$ levels with Zr-filtered Mo Kα radiation. In addition, $h0l$ and $0kl$ timed exposure precession photographic

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[1] Partial fulfillment of requirements for Ph.D. degree, University of Pittsburgh, 1966.

[2] All correspondence should be addressed to this author. Research performed at the University of Pittsburgh.

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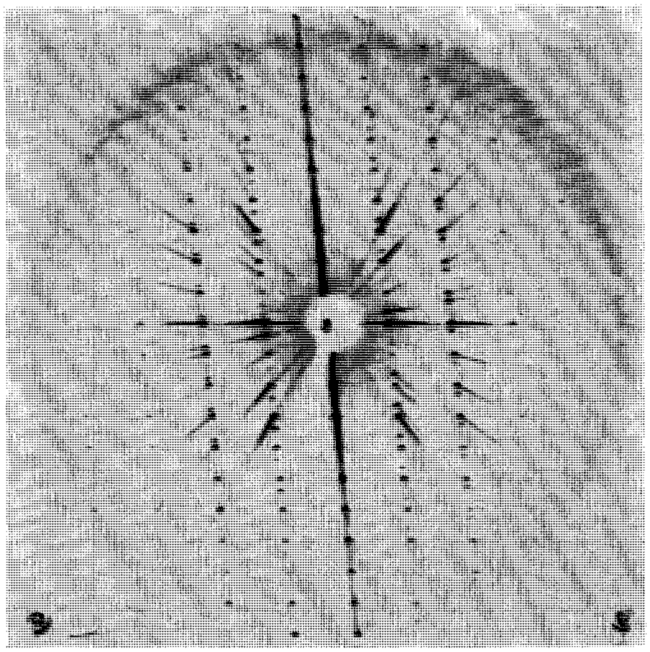

Figure 1.—Precession photograph of *h0l* zone of $Ag(N_2C_4H_4)\cdot NO_3$: a^*, vertical; c^*, horizontal. The a^* axis reflections are all $h = 2n$, with reflections from the twins superposed. With this information all the other reflections can be readily identified.

data were obtained and used for preliminary scaling of the three-dimensional data for Patterson and electron density calculations. A total of 735 independent *hkl* data was visually estimated with a calibrated strip. Lorentz polarization corrections were made, and the intensities were reduced to squared structure factors.

Although crystals were grown under a variety of experimental conditions, it was found that extra reflections always appeared that could not be indexed on the basis of any multiple of the unit cell, Figure 1. The position and intensity distribution of these extra reflections can be explained only by assuming that the apparent single crystals are made up of macroscopic twins related by a 180° rotation about a^*. In general, these twins are not of equal size, and one set of reflections was found to be more intense than that arising from the other twin. The structure was solved by consistently estimating the intensities belonging to only one of the twinned crystals.

Results

Structure Determination.—The short *c* axis means that the plane of the pyrazine ring must be almost normal to the [001] direction since the thickness of the aromatic molecule is 3.40 A.[10]

In space group P2/a with two molecules of $AgNO_3\cdot NC_4H_4N$ per unit cell, the silver atoms must lie on centers of symmetry or on twofold axes of symmetry. The former was rejected, for this would demand that reflections with *h* even be much more intense than with *h* odd; this was not observed. The most reasonable arrangement of atoms is with Ag on the twofold axes at $^1/_4, y, 0$; $^3/_4, \bar{y}, 0$; the center of the aromatic ring on the centers of symmetry at 0, 0, 0; $^1/_2$, 0, 0; the N–O of the nitrate groups on the twofold axes at $^1/_4, y, ^1/_2$; $^3/_4, \bar{y}, ^1/_2$; and the other oxygen atoms of the nitrate group in the general positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 + x, \bar{y}, z$; $^1/_2 - x, y, \bar{z}$. However, in space group Pa, more flexibility is permitted since all the atoms must be in the general positions x, y, z; $^1/_2 + x, \bar{y}, z$. We proceeded to solve the structure in space group Pa. If the true space group were P2/a and not Pa, we should be able to refine to the centrosymmetric case with due consideration of the correlation matrix in the least-squares refinement.

In the noncentric space group Pa the origin is arbitrary, and it was so chosen as to place the *a* glide at $y = 0$. Hence, the Ag(I) ion would have coordinates 0, *y*, 0. Most of the structural information should be available in the projection onto (001) because of the short *c* axis. From an *hk*0 Patterson projection, the *y* coordinate of the Ag atom was readily found; but since any two Ag atoms are related by a center of symmetry, the Ag atom positions could not be used to determine the ring orientation. An attempt was made to solve the *hk*0 Patterson projection as completely as possible. It was found that all the atoms could be located. The first set of structure factors[11] for this projection gave a disagreement index, R,[12] of 0.28. After two Fourier cycles R was reduced to 0.20, and the rings rotated somewhat during this process. Several difference map cycles reduced the R factor to 0.15.

Little could be learned about the *z* coordinates from the 0*kl* Patterson due to the overlapping peaks, but the *h*0*l* Patterson indicated that the nitrate group with nitrogen and one oxygen at $z \sim {}^1/_2$ was tipped. Several Fourier and difference Fourier cycles brought the *h*0*l* agreement to 0.25. At this point three-dimensional data were available, structure factors were computed using the atomic parameters from the two-dimensional data, and R was found to be 0.20. After two Fourier cycles, R was reduced to 0.17.

The structure was refined by complete-matrix least squares on the IBM 7090.[13] The function minimized was $\sum\omega(F_o - F_c)^2$. The weighting scheme was that of Hughes[14] with $4F_{\min} = 12$. In attempting to refine the structure in space group Pa, it was found there were large correlations (>0.7) between atoms that would be symmetry related in P2/a. The refinement was continued in Pa, but without varying simultaneously the correlated atoms. It was found that the space group was P2/a within less than a standard deviation. The refinement was completed in space group P2/a. The structure was refined (a) with isotropic individual atom temperature factors, (b) with anisotropic Ag atom temperature factors, and (c) with all atoms anisotropic. R factors, weighted R factors, and error of observation of unit weight are tabulated for each refinement in Table II. Anisotropic temperature factors were of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}kl + 2\beta_{13}hl)]$. The β_{12} and β_{23} components for all atoms on the twofold axes (Ag, N, and O of the nitrate) were

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[10] L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

[11] Scattering factors: Ag^+, neutral C, N, O from compilation of J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 204, 211.

[12] $R = \sum||F_o| - |F_c||/\sum|F_o|$.

[13] W. Busing, K. O. Martin, and H. Levy, ORFLS (least-squares program) and ORFFE (distances and errors program).

[14] E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

	F(O)	F(C)
0K0		
2	148	146
3	147	-171
4	137	-125
5	123	-132
6	97	-92
9	44	41
1K0		
2	255	-258
3	241	-307
4	106	-101
6	64	54
7	87	77
8	60	63
9	44	45
2K0		
2	95	-142
3	84	60
4	122	115
5	188	189
6	128	144
8	45	-38
9	58	-64
3K0		
1	139	129
2	223	261
3	237	242
4	86	82
5	83	-75
6	114	-104
7	120	-119
8	59	-63
4K0		
1	180	160
3	133	-134
4	171	-147
5	157	-151
6	89	-100
8	29	23
9	46	50
5K0		
1	133	-117
2	234	-272
3	162	-175
4	135	-121
5	39	35
7	92	86
8	64	67
9	50	61
6K0		
1	269	-302
2	80	-68
3	53	46
4	139	129
5	167	155
6	91	90
8	44	-37
9	47	-38
7K0		
1	93	86
2	257	278
3	263	203
4	183	177
5	43	-35
6	52	-45
7	95	-98
8	42	-40
8K0		
0	197	202
1	209	195
2	64	51
3	41	-25
4	113	-99
5	147	-152
6	92	-99
7	40	-35
8	45	31
9K0		
1	140	-124
2	237	-247
3	137	-132
4	84	-79
5	86	66
6	54	51
7	95	86
8	60	63
9	49	46
10K0		
0	224	-236
1	175	-153
3	120	117
4	132	130
5	141	135
6	60	63
8	31	-27
9	50	-42
11K0		
1	83	64
2	163	157
3	147	144
4	121	105
6	59	-58
7	95	-93
8	66	-67
12K0		
0	201	214
1	129	135
2	108	90
3	40	-39
4	92	-90
5	132	-140
6	97	-86
13K0		
1	127	-125
2	198	-194
3	181	-168
4	88	-74
6	55	47
7	50	53
9	55	17
14K0		
0	214	-227
1	134	-123
2	75	-61
3	71	61
4	80	77
5	95	91
6	66	68
7	45	23
8	53	2
15K0		
1	101	86
2	140	130
3	131	128
4	62	60
6	52	-50
7	58	-71
16K0		
0	150	156
1	90	86
2	51	43
3	74	-63
4	101	-108
5	105	-115
6	66	-72
8	50	29
17K0		
1	65	-67
2	127	-110
3	109	-111
4	57	-59
6	62	55
7	67	77
18K0		
0	149	-145
1	100	-95
2	51	-39
3	37	39
4	66	76
5	71	78
6	60	62
19K0		
1	102	95
2	143	141
3	105	108
4	54	53
7	53	-48
20K0		
0	136	139
1	106	105
2	57	45
4	65	-70
5	70	-76
6	56	-52
21K0		
1	51	-43
2	89	-88
3	92	-88
4	70	-73
7	58	64
22K0		
0	102	-101
1	69	-76
3	34	40
4	68	75
5	76	78
23K0		
1	58	65
2	98	100
3	56	66
24K0		
0	93	89
1	61	64
4	61	-53
5	52	-62
25K0		
1	51	-46
2	73	-81
3	72	-74
6	26	29
26K0		
0	81	-95
1	76	-72
5	63	62
27K0		
2	53	71
3	59	63
28K0		
0	77	79
1	37	54
2	67	17
5	26	-48
0K1		
2	45	41
3	69	-56
4	136	-147
5	87	-90
6	36	-34
1K1		
2	190	-241
3	121	-124
4	104	-94
6	51	45
7	54	57
8	40	47
-1K1		
2	152	171
3	148	146
4	128	111
5	45	38
6	62	-56
7	61	-67
8	47	-55
2K1		
2	55	-31
4	125	131
5	120	122
6	77	71
7	43	36
-2K1		
2	94	-87
3	33	24
4	141	140
5	124	132
6	77	75
7	37	21
8	43	-32
9	46	-40
3K1		
1	112	112
2	154	173
3	107	113
4	91	83
5	32	-21
6	85	-92
7	111	-91
8	44	-54
-3K1		
2	150	-169
3	152	-153
4	31	-30
6	110	107
7	67	75
8	48	57
4K1		
0	116	111
1	178	193
3	94	-69
4	141	-149
5	101	-107
6	50	-48
-4K1		
0	170	188
1	116	119
2	65	46
3	106	-98
4	136	-136
5	90	-94
6	64	-58
7	42	-27
9	45	38
5K1		
1	132	-138
2	153	-156
3	116	-117
4	70	-60
6	52	43
7	55	49
8	49	59
-5K1		
1	171	175
2	131	131
3	168	164
4	59	39
5	59	46
6	79	-68
7	55	-54
8	59	-62
6K1		
0	198	-206
1	184	-195
2	96	-74
3	40	38
4	118	108
5	90	91
6	53	52
-6K1		
0	216	-252
1	174	-179
2	148	-124
3	37	46
4	129	133
5	101	105
6	66	65
7K1		
1	146	127
2	152	148
3	165	170
4	82	72
6	72	-71
7	57	-52
8	45	-38
-7K1		
1	153	-137
2	129	-129
3	185	-187
4	90	-78
5	63	-48
6	73	72
7	59	61
8	43	43
8K1		
0	134	133
1	115	106
2	103	77
4	96	-91
5	97	-98
6	70	-71
-8K1		
0	158	157
1	149	135
2	97	69
3	37	-29
4	113	-112
5	83	-86
6	70	-72
9K1		
1	127	-115
2	115	-111
3	126	-121
6	63	66
7	48	51
8	44	56
-9K1		
1	167	156
2	142	156
3	122	122
6	70	-67
7	58	-60
10K1		
0	146	-162
-10K1		
0	122	-119
1	110	-103
-10K1		
1	147	-132
3	94	82
-10K1		
3	74	57
4	121	115
-10K1		
4	131	133
5	68	74
-10K1		
5	90	88
6	54	55
11K1		
1	95	80
2	90	91
3	115	112
4	51	41
6	60	-56
7	51	-54
-11K1		
1	90	-68
2	110	-103
3	110	-108
4	96	-82
6	58	58
7	69	80
8	45	53
12K1		
0	113	107
1	116	104
2	75	56
4	80	-78
5	77	-83
6	63	-64
-12K1		
0	124	117
1	154	155
2	60	42
4	111	-106
5	90	-94
6	54	-54
13K1		
1	103	-90
2	124	-121
3	112	-117
4	55	-51
-13K1		
1	128	112
2	149	158
3	114	110
4	71	61
6	40	-35
14K1		
0	123	-120
1	115	-114
4	66	73
5	49	55
-14K1		
0	121	-119
1	140	-135
2	40	-28
4	76	76
5	62	70
6	43	44
15K1		
1	48	62
2	92	88
3	65	75
4	43	39
-15K1		
1	77	-71
2	106	-110
3	95	-93
4	61	-57
6	49	53
7	45	56
16K1		
0	63	75
1	86	82
4	80	-82
5	66	-74
-16K1		
0	93	89
1	94	93
4	102	-93
5	96	-96
17K1		
1	47	-47
2	80	-77
3	63	-73
-17K1		
1	64	60
2	90	87
3	58	83
7	51	-48
18K1		
0	61	-72
1	90	-75
5	47	56
-18K1		
0	111	-109
1	105	-90
4	50	66
5	64	64
19K1		
1	64	64
2	90	90
3	64	72
-19K1		
1	95	-82
2	130	-107
3	65	-96
20K1		
0	91	90
-20K1		
0	121	99
1	68	80
-20K1		
1	87	84
4	52	-57
5	51	-49
-20K1		
5	60	-64
21K1		
2	48	-53
3	65	-63
-21K1		
2	67	66
3	49	84
-22K1		
0	95	-87
1	68	-68
5	56	56
23K1		
2	53	60
-23K1		
1	56	-58
2	58	-73
-24K1		
0	53	65
1	53	58
-25K1		
2	51	64
-26K1		
0	63	-73
1	55	-67
0K2		
2	85	66
3	84	-70
4	92	-95
5	102	-102
6	66	-68
1K2		
2	193	-219
3	162	-180
4	64	-58
5	50	25
-1K2		
2	144	169
3	151	165
4	144	137
7	89	-84
2K2		
1	51	-61
2	89	-77
3	58	55
4	75	79
5	116	121
6	94	98
-2K2		
2	41	-33
3	44	36
4	107	110
5	145	147
6	84	92
3K2		
1	72	72
2	127	124
3	160	167
4	61	60
6	82	-83
7	91	-93
-3K2		
2	217	-236
3	121	-121
4	67	-76
5	113	88
6	59	53
7	82	89
4K2		
0	215	254
1	73	75
2	58	55
3	124	-100
4	114	-111
5	118	-120
6	67	-74
-4K2		
1	127	154
2	50	-26
3	129	-72
4	104	-94
5	116	-114
6	67	-72
5K2		
1	103	-102
2	156	-145
3	151	-142
4	48	-55
7	65	55
-5K2		
1	80	69
2	204	212
3	134	131
4	123	113
7	77	-78
6K2		
0	256	-255
1	144	-132
2	90	-72
3	58	52
4	71	73
5	84	87
6	68	66
-6K2		
0	225	-248
1	200	-199
2	96	-67
3	44	39
4	110	95
5	142	146
6	66	72
7K2		
1	101	97
2	181	170
3	156	152
4	99	87
-7K2		
1	66	-62
2	184	-184
3	166	-163
4	136	-125
7	68	66
8K2		
0	141	138
1	105	102
2	77	58
4	78	-76
5	111	-109
6	74	-77
-8K2		
0	237	237
1	140	127
2	62	50
3	71	-65
4	74	-70
5	112	-115
6	72	-74
9K2		
1	52	-62
2	120	-126
3	83	-87
4	79	-66
-9K2		
1	139	121
2	186	188
3	152	143
5	67	-47
6	69	-61
7	67	-59
10K2		
0	158	-154
-10K2		
0	185	-197
1	115	-110
-10K2		
1	70	-72
2	62	-44
3	102	83
-10K2		
3	97	79
4	95	100
-10K2		
4	97	90
5	88	81
-10K2		
5	126	123
6	75	81
11K2		
1	60	65
2	131	127
3	82	81
4	68	62
-11K2		
1	57	-51
2	112	-105
3	145	-151
4	84	-79
6	65	64
7	73	83
12K2		
0	106	103
1	105	94
2	67	54
5	87	-91
6	70	-62
-12K2		
0	225	231
1	137	115
2	87	66
3	63	-58
4	87	-91
5	74	-104
6	65	-75
13K2		
1	65	-65
2	132	-126
3	101	-101
4	74	-75
-13K2		
1	130	114
2	150	162
3	145	147
4	62	51
14K2		
0	146	-139
1	99	-95
4	74	60
-14K2		
0	182	-184
1	107	-108
2	66	-50
6	76	78
15K2		
1	69	55
2	91	89
3	66	66
-15K2		
1	66	-68
2	125	-123
3	122	-123
4	69	-70
16K2		
0	96	97
4	80	-66
-16K2		
0	117	126
1	90	89
4	100	-101
5	97	-103
17K2		
2	81	-78
3	71	-73
-17K2		
2	98	111
3	80	88
4	70	58
18K2		
0	79	-84
-18K2		
0	153	-144
1	125	-107
4	74	75
19K2		
2	88	82
-19K2		
1	82	-77
2	152	-135
3	93	-98
4	75	-64
-20K2		
0	126	112
1	94	94
-21K2		
2	83	97
3	85	87
-22K2		
0	135	-119
1	83	-78
-23K2		
2	84	-91
-24K2		
0	89	87
-26K2		
0	98	-101
0K3		
1	83	96
2	52	46
4	62	-60
5	44	-50
1K3		
1	91	-95
2	97	-104
3	83	-82
-1K3		
2	41	52
3	88	96
4	61	49
5	64	40
6	43	-43
2K3		
0	34	-58
1	76	-75
4	62	59
5	53	54
-2K3		
1	52	-66
2	41	-42
3	43	34
4	85	78
5	66	65
3K3		
1	42	39
2	51	62
3	57	60
4	41	39
6	59	-48
-3K3		
1	82	-94
2	70	-78
3	80	-81
6	58	54
4K3		
0	41	53
1	82	86
3	38	-26
4	83	-76
5	67	-63
-4K3		
0	51	81
1	47	59
3	45	-35
4	66	-70
5	44	-44
6	49	-41
5K3		
1	60	-52
2	77	-78
3	55	-55
4	42	-35
-5K3		
1	72	74
2	68	75
3	90	88
4	40	35
6K3		
0	75	-73
1	111	-96
4	47	45
-6K3		
0	88	-91
1	115	-107
2	63	-45
4	78	81
5	61	61
7K3		
1	71	58
2	98	86
3	76	70
-7K3		
1	64	-62
2	73	-79
3	80	-78
4	69	-56
5	44	-22
8K3		
0	40	48
1	77	66
4	55	-49
5	60	-54
-8K3		
0	80	78
1	110	106
4	71	-73
5	45	-45
9K3		
3	51	-51
-9K3		
1	94	79
2	104	102
3	59	57
10K3		
0	65	-69
1	51	-54
-10K3		
1	75	-75
3	57	39
4	64	55
-10K3		
4	78	71
5	73	67
11K3		
1	55	49
2	47	56
3	58	53
-11K3		
1	41	-39
2	61	-67
3	66	-60
4	64	-54
-12K3		
0	108	89
1	118	99
4	79	-66
5	52	-57
13K3		
3	77	-63
-13K3		
1	89	73
2	93	91
3	75	66
5	54	12
14K3		
0	56	-65
1	62	-53
-14K3		
0	75	-75
1	79	-73
2	49	-35
-15K3		
1	64	-50
2	53	-66
3	71	-74
5	57	-8
-16K3		
0	54	63
4	58	-61
-17K3		
1	55	51
-18K3		
0	91	-84
1	68	-64
4	62	55
-19K3		
1	60	-52
2	67	-64
3	61	-69
-20K3		
1	61	58

[a] $F(\mathrm{C}) = 10F(\mathrm{calcd})$. To put $F(\mathrm{C})$ on an absolute scale: $F(\mathrm{calcd})_{\mathrm{absolute}} = F(\mathrm{calcd})/\text{scale factors}$.

required to be zero by Levy's rules.[15] The scale factors were not varied during the anisotropic refinement but were readjusted after the anisotropic refinement was complete. The maximum coordinate shift for the last cycle of refinement was found to be less than 3×10^{-6} and 3×10^{-4} of a cell edge for Ag and the light atoms, respectively.

A three-dimensional difference map computed at the end of the isotropic refinement indicated appreciable anisotropy in the thermal motion of the silver atom. A significant decrease in the disagreement index (0.158 to 0.095) was observed upon allowing the Ag atom to refine anisotropically. If one examines the β_{ii} of the Ag atom, one finds: $\beta_{11} \rightarrow B = 0.42$ A^2, $\beta_{22} \rightarrow B = 2.05$ A^2, $\beta_{33} \rightarrow B = 1.61$ A^2.[16] This corresponds to a greater thermal motion in directions normal to the chain—qualitatively the result one would expect for a chain structure. Further, all of the ring atoms have approximately the same B factors (0.4–0.8 A^2).

For these reasons we feel there is some justification for the anisotropic Ag refinement. Hamilton's R factor test[17] would also indicate a significance to the Ag anisotropic refinement, but there exists sufficient systematic error that this test may not be applicable. The effect of various sources of systematic error such as absorption, anamolous dispersion, twinning, and data from only one rotation axis puts the absolute magnitude of all the B factors in error and probably makes them all somewhat low. On the other hand, there is very little change in disagreement index (0.095–0.091) upon allowing anisotropic temperature factors for the light atoms. There was, also, virtually no change in either the coordinates or standard deviations in going to the complete anisotropic refinement from the Ag-

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(15) H. A. Levy, *Acta Cryst.*, **9**, 679 (1956).

(16) This assumes that $\beta_{ij} = 0$, $i \neq j$; the error in this assumption does not appreciably alter the qualitative discussion of the chain motion.

(17) W. C. Hamilton, *Acta Cryst.*, **18**, 502 (1965).

TABLE II

POSITIONAL AND TEMPERATURE PARAMETERS AND ERRORS; $\sigma' = \sigma \times 10^4$

Atom	x/a	$\sigma'(x)/a$	y/b	$\sigma'(y)/b$	z/c	$\sigma'(z)/c$	B, A^2 [a]
Ag	0.2500	...[b]	0.1015	3	0.0000	...[b]	0.76 ± 0.03
O_1	0.3168	9	0.4434	19	0.3815	42	2.41 ± 0.43
O_3	0.2500	...[b]	0.7393	25	0.5000	...[b]	3.56 ± 0.84
N (nitrate)	0.2500	...[b]	0.5413	22	0.5000	...[b]	0.41 ± 0.29
N (ring)	0.4033	7	0.0395	19	0.0023	42	0.43 ± 0.20
C_1	0.4645	7	0.1888	19	−0.0746	46	0.58 ± 0.24
C_2	0.5605	8	0.1475	21	−0.0727	49	0.86 ± 0.29

THERMAL PARAMETERS AND STANDARD DEVIATIONS

Anisotropic Temperature Factors of the Form

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

Atom	β_{11}	σ'	β_{22}	σ'	β_{33}	σ'	β_{12}	σ'	β_{13}	σ'	β_{23}	σ'
Ag	0.0005	0	0.0122	3	0.0332	15	0.0000	...[b]	0.0024	2	0.0000	...[b]
O_1	0.0038	6	0.0184	35	0.0266	131	−0.0046	11	0.0047	21	0.0085	49
O_3	0.0060	11	0.0063	34	0.0545	220	0.0000	...[b]	0.0155	33	0.0000	...[b]
N (nitrate)	0.0016	5	0.0020	27	0.0251	419	-0.0000	...[b]	0.0124	23	0.0000	...[b]
N (ring)	0.0011	3	0.0101	26	0.0200	128	−0.0002	8	0.0016	18	−0.0002	47
C_1	0.0012	4	0.0047	24	0.0110	133	−0.0004	9	0.0024	19	0.0009	51
C_2	0.0014	4	0.0097	33	0.0108	137	−0.0009	9	0.0005	20	0.0021	50

Layer	Scale factor	Refinement	R[c]	Weighted R	Error[d]	NV
$hk0$	0.3810 ± 0.0043					
$hk1$	0.2942 ± 0.0029	Complete anisotropic	0.091	0.118	1.13	51
$hk2$	0.3611 ± 0.0035	Mix aniso–iso	0.095	0.123	1.17	25
$hk3$	0.2503 ± 0.0040	Isotropic	0.158	0.187	1.74	22

[a] Ag B factor from isotropic refinement. Light-atom B factors from anisotropic Ag, isotropic light-atom refinement. The atom coordinates, the Ag β_{ij}, and the respective esd's are not significantly different from the complete anisotropic refinement to the mixed anisotropic–isotropic refinement. [b] Must be fixed because of symmetry. [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $[\sum\omega(F_o - F_c)^2/(NO - NV)]^{1/2}$; NV = number of variable parameters; NO = number of observations = 735.

TABLE III[a]

Ag–X distances, A		Intermolecular distances, A	
Ag–N	2.213 ± 0.014	C_2–O_3	3.293 ± 0.021
Ag–O_1	2.720 ± 0.021	C_2'–O_3	3.311 ± 0.023
Ag–O_3	2.943 ± 0.017	O_3–N (ring)	3.514 ± 0.023
		O_1–N (ring)	3.233 ± 0.026
		C_1–O_1	3.224 ± 0.023
Ring distances, A		**Ring angles**	
N–C_1	1.343 ± 0.022	N–C_1–C_2	121.0 ± 1.7
C_1–C_2	1.391 ± 0.022	C_1–C_2–N	122.6 ± 1.7
C_2–N	1.331 ± 0.026	C_2–N–C_1	116.4 ± 1.4
Nitrate distances, A		**Nitrate angles**	
N–O_1	1.246 ± 0.020	O_1–N–O_1'	118.9 ± 2.6°
N–O_3	1.281 ± 0.033	O_1–N–O_3	120.6 ± 1.4°

X–Ag–X	Angles
N–Ag–N′	159.2 ± 0.9°
O_1–Ag–N	81.2 ± 0.6°
O_1–Ag–N′	109.2 ± 0.5°

Deviation from Best Least-Squares Plane for $N_2C_4H_4$[b]

$$aX + bY + cZ + d = 0$$

$a = +0.0452$	N, −0.0051 A
$b = +0.2255$	C_1, +0.0054 A
$c = +0.9732$	C_2, −0.0066 A
$d = -1$	

Dihedral angle between planes defined by N–Ag–N′ and pyrazine ring = 13.8 ± 2.2°.

[a] The errors tabulated in this table are increased by a factor of 1.5 over the values that would be calculated from the data of Table II. We feel that this is a realistic compromise for the neglected systematic errors. [b] Positional standard deviations were used to provide weights for the least-squares plane. X, Y, Z refer to an internal orthogonal coordinate system.

only-anisotropic refinement. Hence, we feel there is no real significance to the light-atom anisotropic model.

Because of the systematic errors mentioned above, no detailed interpretation should be made of even the silver anisotropic temperature factors. For these same reasons our esd's tabulated for the Ag-only-anisotropic and complete anisotropic refinements, both tabulated for completeness in Table II, are probably somewhat optimistic. We report, for the chemical reader, bond-length errors in Table III increased by an arbitrary factor of 1.5 from the values that would be calculated from the data of Table II. This we feel is a realistic assessment of our errors and lies halfway between the esd's of the Ag-only-anisotropic model and the complete isotropic model.

Calculated and observed structure factors, based on the complete anisotropic refinement, are listed in Table I. Final atomic parameters are shown in Table II. Interatomic distances, angles, and errors[13] are seen in Table III.

Description and Discussion of the Structure

The simplest view of the pertinent general structural features is a view down the short c axis, Figure 2. The structure consists of approximately planar-kinked chains of the type $[-Ag-NC_4H_4N-]_x$ with symmetric Ag–N distances of 2.213 ± 0.014 A and N–Ag–N′ angles of 159.2 ± 0.9°. Looking down the chain, the pyrazine rings are alternately canted in opposite directions with a dihedral angle between ring plane and the N′–Ag–N plane of 13.8 ± 2.2°. The next four nearest neighbors to the Ag(I) ion are oxygen atoms of nitrate groups (O_1, O_1') at 2.720 ± 0.021 A and (O_3) at 2.943 ± 0.017 A. These seem like long Ag–O distances for covalent bonding compared to the 2.3–2.5 A

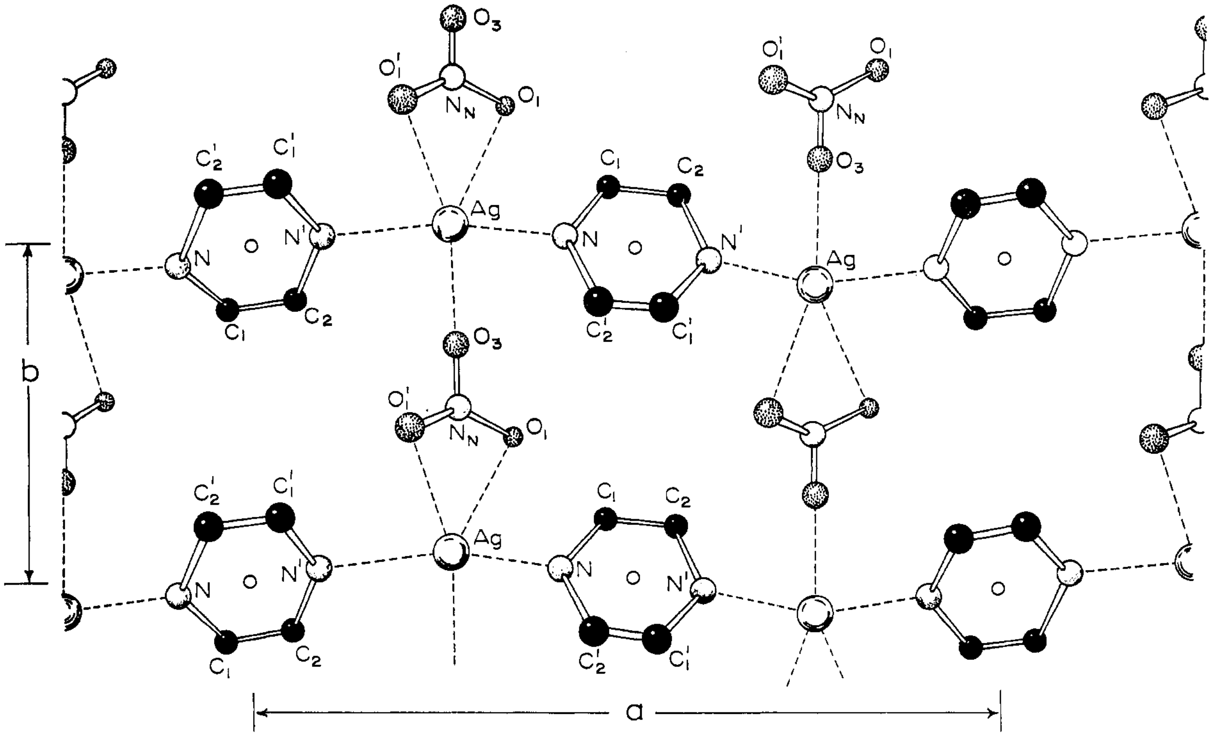

Figure 2.—Perspective view of the $Ag^+ \cdot N_2C_4H_4 \cdot NO_3^-$ structure down the short *c* axis. Dotted lines indicate Ag–X bonds. Since Ag is at $z = 0$ and O_3 is at $z = 1/2$, each Ag has two Ag–O_3 interactions but only one is shown. See also Figure 3.

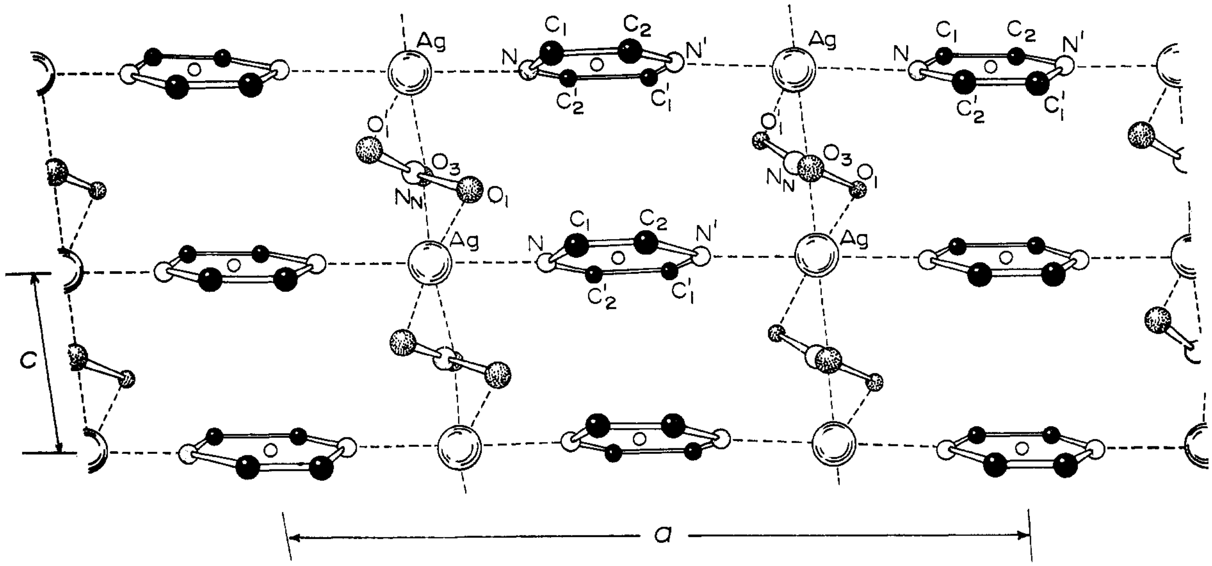

Figure 3.—Perspective view of $Ag^+ \cdot N_2C_4H_4 \cdot NO_3^-$ structure down the *b* axis. Dotted lines indicate Ag–X bonds. In reality N (nitrate) and O_3 are superposed in this direction, but they have been displaced to clarify the Ag–O_3 interaction.

distances generally considered as weak Ag–O bonds.[18–20] It is interesting to note that in a recent redetermination of the structure of $AgNO_3$,[21] Ag–O distances ranging from 2.59 to 2.99 A were found.

It might be argued that π bonding between Ag(I) and the aromatic rings keeps the rings in approximately the same plane, but there is no evidence from the Ag–N distances for π bonding. Our Ag–N distances of 2.213 ± 0.014 A are to be compared with 2.115 ± 0.008 A in AgNCO,[22] 2.561 ± 0.008 A in AgN_3,[23] and 2.05 A in AgCN.[24] It is most likely that packing of planar molecules, both NO_3^- and NC_4H_4N, maintains all of the rings in approximately the same plane.

Within experimental error (see ring angles and least-squares plane deviations, Table III), the aromatic ring is planar. The C–C and C–N bond distances are not significantly different from pyrazine[25] itself (C–N, 1.334; C–C, 1.378; both ±0.015 A). The nitrate

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(19) J. Donohue and W. Shand, Jr., *ibid.*, **69**, 222 (1947).

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(23) Referred to as private communication from Dewing and Hughes in ref 22.

(24) G. Natta and O. Vecchia, *Gazz. Chim. Ital.*, **63**, 439 (1933).

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group is required to be planar in P2/a and, within statistical significance, does not deviate from D_{3h} symmetry. The N–O distances are not significantly different from the generally accepted N–O distance of 1.22 A.[3b,26,27]

Acknowledgment.—We wish to acknowledge financial support from the National Science Foundation, Grant No. GP-1575.

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[26] R. L. Sass, R. Vidale, and J. Donohue, *Acta Cryst.*, **10**, 567 (1957)

[27] We wish to thank one of the referees for his excellent criticism of our original choice of space group Pa. We carefully reexamined the entire problem, and, as seen above, the correct space group seems to be P2/a.

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA GENERALE E INORGANICA,
UNIVERSITA' DI FIRENZE, FLORENCE, ITALY

Infrared Spectra of Substituted Thiocyanate Complexes. The Effect of the Substituent on Bond Type. II

BY I. BERTINI AND A. SABATINI

Received September 7, 1965

Complexes of the general formula $[PdL_2(SCN)_2]$, where L = methyl ester of isonicotinic acid, 4-nitropyridine, or 4-cyanopyridine and L_2 = 5-methyl-*o*-phenanthroline, 5,6- and 4,7-dimethyl-*o*-phenanthroline, 5-chloro-*o*-phenanthroline, 5-methyl-6-nitro-*o*-phenanthroline, 4,7-diphenyl-*o*-phenanthroline, 5-nitro-*o*-phenanthroline, or 4,4'-dimethyl-2,2'-bipyridine, have been prepared. Their infrared spectra were used to establish the bond type Pd–S or Pd–N. The dependence of the bond type on the substituent of the organic ligand is discussed.

Introduction

The problem of which atom of the thiocyanate group is linked to the metal in thiocyanate complexes has been extensively studied by analyses of infrared spectra.[1-3]

Various authors[1,3,4] have noticed that the value of the C–S stretching frequency is diagnostic of the type of bonding: *ca.* 700 cm^{-1} for S-bonded thiocyanate compounds, 760–880 cm^{-1} for N-bonded thiocyanate complexes. Furthermore, the other vibration modes of the NCS group have been studied, and it has been concluded that, although the C–N stretching frequency does not have a shift characteristic for S- and N-bonded complexes,[1] the NCS bending frequency is still indicative of the type of bonding:[3,5] 450–490 cm^{-1} for N-bonded thiocyanates; 400–440 cm^{-1}, often with weaker bands at higher frequencies, for S-bonded thiocyanate complexes.

Turco and Pecile[4] have studied complexes in which as well as the thiocyanate group one or more organic ligands are present, and they have found that substituting two of the NCS ions in the S-bonded complexes $[Pt(SCN)_4]^{2-}$ and $[Pd(SCN)_4]^{2-}$ with two trialkylphosphines causes isomerization from M–S to M–N bonding. Subsequently, Basolo and Burmeister[6,7] have found that $[Pd(bipy)(NCS)_2]$ and $[Pd(As(C_6H_5)_3)_2(NCS)_2]$ both give linkage isomers, and they succeeded in separating them. These authors[4,6,7] have drawn these conclusions by analyzing only the values of the C–S stretching frequency.

In one of our previous papers[8] we drew attention to the fact that the assignment of the band due to C–S stretching may be incorrect, if the infrared investigation is not extended so far as the region of the NCS bending frequencies. In fact, the first harmonic of the NCS deformation frequency of an S-bonded thiocyanate compound lies in the range 820–880 cm^{-1} and can therefore be assigned to the C–S stretching, diagnostic of an N-bonded thiocyanate complex. Furthermore we drew attention to the fact that in the compounds $[PdL_2(NCS)_2]$ the C–N stretching also assumes characteristic forms and values: >2100 cm^{-1} and sharp for S-bonded thiocyanates; ≤ 2100 cm^{-1} and broad for N-bonded thiocyanates.

In this article we intend to study the effect of variously substituted organic ligands, whose donor atom is an aromatic nitrogen, on the type of bonding of the thiocyanate group. The possible variation of the type of bonding of the thiocyanate group as a function of the substituent of the organic base may help to identify parameters characteristic of the ligand which may be correlated with the bonding type Pd–S or Pd–N.

Experimental Section

The following organic ligands were prepared according to the methods described in the literature: 5-methyl-*o*-phenanthroline, 5,6-dimethyl-*o*-phenanthroline, 5-chloro-*o*-phenanthroline,[9] 5-nitro-*o*-phenanthroline,[10] 4,4'-dimethyl-2,2'-bipyridine,[11] and 4-nitropyridine.[12] The other ligands are commercially available.

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