M–M force constant is quite close to the approximate constant calculated with neglect of ligands from the A_1 frequency: $f_{M-M} = {}^1/_4 m_M \lambda^{A_1}_{M-M}$. In general it appears that neglect of carbonyl ligands produces negligible errors in the calculation of metal–metal force constants for third-row transition elements, and even in the first row the error does not exceed 30%. Such calculations are quite simple and, in the absence of normal-coordinate analyses, may be expected to yield useful estimates. When heavier ligands, such as halides, are present, mixing is apt to be severe[18] and their neglect would lead to more serious errors.

Examination of the metal–metal force constants for the seven polynuclear carbonyls listed in Table V reveals some notable trends. Within a given row or period f_{M-M} values increase with increasing atomic number, in accord with expectation based on chemical stabilities and mass spectral fragmentation patterns.[19–21] Moreover the force constants for the dinuclear carbonyls correlate satisfactorily with M–M bond dissociation energies estimated from electron impact measurements.[22] In particular the exceptional stability of the Mn–Re bond is revealed in both quantities, although it is more pronounced in the D_0 estimates. For the third-row transition carbonyls the increase of f_{M-M} from $Re_2(CO)_{10}$ to $Os_3(CO)_{12}$ to $Ir_4(CO)_{12}$ correlates with decreasing metal–metal bond length. However force constants for different geometries are not strictly comparable because the force fields have different forms. Indeed the very large increase from f_{Os-Os} to f_{Ir-Ir} is out of proportion to the decrease in bond length and no doubt reflects the greater complexity of the $Ir_4(CO)_{12}$ force field. The A_1 symmetry force constant for $Ir_4(CO)_{12}$, 1.30 mdyn/Å, seems to provide a more reasonable basis for comparison.

Experimental Section

$Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from Alfa Inorganics, Inc., and were used as received. $MnRe(CO)_{10}$ was prepared according to Flitcroft, *et al.*,[23] and purified by sublimation. The purity of the compounds was verified by infrared spectroscopy in the carbonyl region using a Beckman IR12.

Raman spectra were obtained with a spectrometer[24] equipped with an He–Ne laser source at a nominal power of 50 mW (6328 Å). The samples were held in a 1-mm thin-walled X-ray capillary placed perpendicular to the laser beam. Scattered light was collected at 90°.

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The Crystal and Molecular Structure of *trans*-Dichlorotetrakis(thiourea)cobalt(II)

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The crystal structure of *trans*-dichlorotetrakis(thiourea)cobalt(II), $Co[SC(NH_2)_2]_4Cl_2$, has been determined by three-dimensional X-ray diffraction techniques from 885 reflections measured with an automatic diffractometer. The compound crystallizes in the tetragonal space group $P4_2/n$ with $a = b = 13.508 \pm 0.007$ Å, $c = 9.106 \pm 0.005$ Å, $D_m = 1.72$ g/cm^3, and $D_c = 1.72$ g/cm^3 for $Z = 4$. The structure, including hydrogen atoms, was refined by least-squares methods to a conventional R of 0.045. The structure consists of discrete molecules interconnected with hydrogen bonds. However, it is not isostructural with *trans*-$Ni[SC(NH_2)_2]_4Cl_2$ as previously reported. The cobalt atom is located on a center of symmetry and is octahedrally coordinated to four sulfur and two chlorine atoms. The two independent Co–S distances are 2.502 and 2.553 Å, both ±0.006 Å; the Co–Cl distance is 2.469 ± 0.002 Å. The S–C (1.712 and 1.730 Å, both ±0.013 Å) and C–N (average 1.311 Å with individual esd's of ±0.016 Å) bond lengths do not differ significantly from each other nor from values reported for free thiourea and other thiourea complexes. The thiourea groups, including hydrogens, are planar well within experimental error. $M^{II}[SC(NH_2)_2]_4Cl_2$ is an isomorphous series when M is Co, Fe, Mn, and Cd.

Introduction

As a part of the systematic investigation of metal–sulfur bonds in thiourea complexes, we have investigated the crystal structure of *trans*-dichlorotetrakis(thiourea)cobalt(II), $Co(tu)_4Cl_2$ [tu = $SC(NH_2)_2$]. As a ligand thiourea has several modes of binding to a metal atom, and thiourea complexes of the transition metals have exhibited some interesting and unusual properties.[2] $Co(tu)_4Cl_2$, as well as the analogous iron, manganese,

(1) Author to whom correspondence should be addressed.

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TABLE IA

OBSERVED STRUCTURE FACTORS[a]

* H	0	0 *
2	514	550
4	192	173
6	559	564
8	778	795
10	196	190
12	319	315
14	167	170
16	148	140
18	97	103
20	118	116
* H	1	0 *
3	86	92
7	62	-70
* H	2	0 *
2	214	199
4	631	654
6	410	423
8	613	621
10	142	130
14	240	240
16	299	291
* H	4	0 *
2	841	919
4	1136	1177
6	185	181
8	182	173
10	456	449
12	338	326
14	174	172
16	125	129
* H	5	0 *
1	106	98
3	79	-81
* H	6	0 *
2	407	408
4	327	335
6	295	282
8	253	246
10	395	392
12	230	230
18	203	206
* H	7	0 *
3	62	-62
* H	8	0 *
2	217	195
4	231	220
6	564	569
8	365	356
10	104	97
12	181	179
14	206	212
16	108	112
* H	10	0 *
2	200	185
4	347	334
6	329	332
8	231	231
12	136	137
14	214	210
16	87	83
* H	11	0 *
3	51	55
* H	12	0 *
2	510	509
4	299	288
6	72	-59
8	228	222
10	286	284
12	124	151
16	92	90
* H	14	0 *
2	89	92
4	173	180
6	111	109
8	162	165
10	197	170
16	96	100
* H	16	0 *
4	194	189
6	278	274
12	121	121
14	119	123
* H	18	0 *
2	145	151
4	58	56
6	91	96
8	61	61
14	70	70
* H	20	0 *
2	171	174
8	100	96
* H	0	1 *
1	101	91
3	50	57
8	58	-55
11	59	-51
* H	1	1 *
1	463	-493
2	55	-49
3	357	331
4	67	-61
5	53	49
6	103	-99
7	591	-589
9	362	-355
10	76	-79
11	197	184
13	80	-79
14	64	-58
15	192	-187
* H	2	1 *
1	97	-98
3	66	-63
7	108	-98
9	79	-77
15	65	-62
* H	3	1 *
1	455	-451
2	191	-180
3	389	-372
4	64	53
5	359	-325
6	160	-148
7	157	-145
8	44	-44
9	171	-161
10	85	-86
13	170	-165
14	102	-101
15	183	-183
17	70	-70
* H	4	1 *
1	73	66
3	56	49
4	74	-69
5	52	38
8	60	83
10	54	-42
* H	5	1 *
1	215	-203
2	181	-178
3	520	-526
4	42	33
5	265	-255
6	124	-117
7	295	274
8	53	-52
9	210	-194
10	88	-85
11	397	-392
14	66	-68
15	116	104
17	93	-94
19	77	-85
* H	6	1 *
1	74	72
5	66	-59
11	54	-51
* H	7	1 *
1	90	-98
2	75	-76
4	75	-76
5	281	-273
6	67	-71
7	239	-231
9	103	-95
10	119	-121
11	127	-125
17	92	-110
19	83	-98
* H	8	1 *
3	55	48
4	54	56
5	101	100
8	52	-47
* H	9	1 *
1	131	-124
3	116	111
4	81	-77
5	143	-142
6	91	-91
7	405	-403
10	55	-53
11	78	73
12	56	-61
13	130	-145
15	145	-155
* H	10	1 *
1	78	78
2	49	-51
* H	11	1 *
1	258	-249
2	78	-74
3	385	-381
6	81	-80
8	57	-61
9	90	-90
11	84	-90
13	75	-93
15	69	-83
* H	12	1 *
1	56	62
* H	13	1 *
1	141	-139
2	82	-77
3	143	-146
9	213	-213
10	65	-64
11	136	-137
17	69	-89
* H	15	1 *
2	57	-58
5	185	-184
6	59	-58
7	107	-106
* H	17	1 *
5	134	-137
7	58	-51
13	111	-111
* H	19	1 *
1	130	-131
3	79	-77
* H	21	1 *
9	78	-80
* H	0	2 *
0	666	713
1	131	171
2	195	-177
3	200	-233
4	788	-774
5	226	211
6	68	56
7	84	-68
8	204	196
10	65	-57
11	49	-53
13	69	63
15	78	-74
* H	1	2 *
2	62	-62
3	98	85
4	101	-83
5	43	-41
6	59	-48
9	52	50
* H	2	2 *
1	273	266
2	109	94
3	330	-310
5	109	92
6	207	188
8	221	206
10	64	-56
11	65	-63
12	165	-161
13	57	54
14	127	124
16	138	137
* H	3	2 *
2	43	-42
6	81	73
* H	4	2 *
1	50	59
2	241	244
4	331	299
5	39	-46
6	245	-227
7	46	-48
8	262	-244
9	49	54
10	165	164
12	60	59
* H	5	2 *
2	48	-37
3	71	-71
12	50	-43
* H	6	2 *
1	42	-40
2	171	150
3	69	64
5	62	-62
7	49	-49
10	210	208
12	69	70
14	103	-100
18	102	124
* H	7	2 *
2	209	200
10	63	61
12	61	59
* H	8	2 *
2	211	-204
3	44	-37
4	235	-232
6	241	240
8	73	64
10	135	-128
14	66	83
* H	9	2 *
1	56	-58
2	110	-109
4	75	-72
6	58	70
* H	10	2 *
3	67	-61
4	70	72
6	145	149
7	53	-48
10	93	-100
14	80	129
* H	11	2 *
5	57	-63
* H	12	2 *
1	51	54
2	240	230
3	61	-61
6	235	-229
10	139	140
* H	13	2 *
3	54	-48
* H	14	2 *
8	63	59
10	83	87
* H	16	2 *
2	138	-131
6	141	141
10	76	-72
* H	18	2 *
2	85	71
* H	0	3 *
1	96	75
2	55	54
3	67	64
7	63	60
15	74	75
* H	1	3 *
1	569	-594
2	107	106
3	74	-72
5	130	-121
7	662	-651
8	125	119
9	376	-358
10	55	51
13	108	-109
15	257	-255
17	81	-81
* H	2	3 *
1	221	-214
2	97	96
5	148	136
11	112	107
13	58	57
* H	3	3 *
1	298	-272
2	97	-98
3	554	-562
4	198	182
5	281	-254
7	240	-229
9	178	-176
10	91	89
11	99	-97
12	73	75
13	115	-117
15	188	-191
16	77	78
* H	4	3 *
1	69	66
3	49	45
* H	5	3 *
1	258	-236
2	97	-94
3	642	-654
4	148	143
5	311	-302
6	88	85
9	188	-180
10	53	57
11	420	413
12	95	97
13	105	-104
17	85	-102
19	80	-113
* H	6	3 *
3	125	-117
5	128	-129
7	89	94
9	90	87
* H	7	3 *
1	212	-204
2	121	115
3	58	-59
5	236	-232
6	137	129
7	281	-291
8	64	68
9	124	-129
11	156	-164
13	54	-54
14	82	110
* H	8	3 *
1	95	-90
5	75	82
8	61	-36
9	88	-95
* H	9	3 *
1	168	-155
2	176	167
3	55	-57
4	67	-63
5	238	-234
6	53	54
7	396	-392
8	77	81
9	59	-63
10	89	103
13	105	-163
15	113	-176
* H	10	3 *
5	57	-50
6	52	61
7	66	-64
* H	11	3 *
1	263	-258
2	53	59
3	368	-372
4	75	71
5	52	-63
7	63	-72
9	108	-113
10	92	93
11	86	-112
* H	12	3 *
5	54	-47
* H	13	3 *
1	158	-157
3	222	-221
4	81	80
9	191	-193
11	161	-159
* H	14	3 *
1	100	-100
3	70	-71
* H	15	3 *
5	159	-162
7	137	-139
* H	17	3 *
3	84	-76
5	130	-130
7	84	-89
13	101	-104
* H	21	3 *
9	69	-74
* H	0	4 *
0	907	860
2	467	462
4	73	67
5	96	99
6	479	473
8	484	464
9	88	-84
10	228	220
12	120	116
13	61	61
14	163	162
16	89	89
18	113	116
* H	1	4 *
1	75	65
2	170	159
3	62	52
4	70	62
5	68	-72
6	58	36
8	100	94
10	75	83
* H	2	4 *
2	458	458
3	107	-98
4	301	284
6	458	443
7	163	161
8	411	397
9	76	-71
10	162	155
12	71	78
13	78	79
14	249	253
16	174	186
* H	3	4 *
2	222	-209
4	149	-149
5	51	50
12	52	-50
* H	4	4 *
2	525	524
3	146	140
4	673	657
5	130	-122
6	204	191
7	92	84
8	144	135
10	329	322
12	212	209
14	94	98
15	61	67
16	103	114
* H	5	4 *
2	60	58
3	62	-62
4	154	150
6	70	71
* H	6	4 *
1	107	-95
2	378	373
3	217	216
4	377	382
5	93	-94
6	163	159
8	173	178
9	61	60
10	330	333
11	71	76
12	226	233
* H	7	4 *
2	70	66
6	141	-143
8	84	-87
12	69	74
* H	8	4 *
2	89	85
3	76	80
4	134	129
5	52	59
6	442	446
7	56	49
8	290	302
11	57	57
12	83	110
14	95	160
* H	9	4 *
2	88	-87
3	71	74
6	105	103
8	90	94
* H	10	4 *
2	285	277
4	215	210
5	78	72
6	268	267
8	163	170
* H	11	4 *
2	67	-71
* H	12	4 *
1	97	105
2	359	356
4	204	204
8	118	120
10	240	246
12	79	83
* H	13	4 *
2	61	60
4	73	73
* H	14	4 *
2	134	134
4	124	125
6	105	112
8	107	114
10	150	148
* H	16	4 *
4	128	131
6	199	204
8	65	65
12	74	78
14	84	82
* H	18	4 *
6	61	63
* H	20	4 *
8	80	89
* H	0	5 *
1	62	-76
11	87	-85
13	71	-73
* H	1	5 *
1	233	-232
2	96	100
3	114	107
5	68	54
6	127	-126
7	258	-249
9	105	-99
11	151	141
12	86	-89
15	130	-132
* H	2	5 *
1	147	-140
2	91	92
3	94	101
5	105	98
7	71	-73
9	90	-90
* H	3	5 *
1	76	71
2	112	-111
3	230	-221
5	80	-70
6	69	-59
8	105	-102
9	108	-108
14	86	-87
15	97	-99
* H	4	5 *
1	142	139
2	60	-62
5	77	-76
7	68	-62
15	58	-61
* H	5	5 *
1	77	-74
2	172	-172
3	286	-277
5	115	-110
7	163	147
8	104	-109
10	66	-63
11	160	-157
* H	6	5 *
1	63	56
3	104	-107
5	49	-42
9	66	64
11	71	-68
* H	7	5 *
1	91	-95
3	178	166
4	119	-112
5	103	-100
7	107	-107
9	101	-104
10	89	-86
* H	8	5 *
1	56	-56
3	56	53
5	95	99
9	69	-69
* H	9	5 *
1	86	-86
2	80	75
3	85	79
4	129	-131
5	160	-163
6	69	-68
7	119	-116
11	84	98
* H	10	5 *
1	58	57
3	82	79
7	55	-56
* H	11	5 *
1	118	-121
3	119	-116
6	59	-62
8	63	-64
9	84	-93
* H	12	5 *
1	58	57
* H	13	5 *
1	106	-109
3	107	-109
8	84	-85
9	91	-101
* H	15	5 *
5	78	-81
7	63	-66
* H	17	5 *
5	84	-85
* H	0	6 *
0	257	246
2	57	60
3	63	-66
5	123	119
6	118	116
7	65	-61
8	188	183
9	99	-96
15	58	-59
* H	1	6 *
2	44	45
4	107	-103
6	101	-105
* H	2	6 *
1	62	51
3	193	-182
4	56	-50
7	57	52
8	113	109
9	91	-85
10	54	-49
11	60	-66
14	89	93
* H	3	6 *
4	86	-87
6	79	84
8	105	105
12	100	-107
* H	4	6 *
1	136	136
2	99	99
4	288	285
5	104	-103
10	79	78
11	85	-87
12	81	78
* H	5	6 *
4	77	76
8	90	-94
* H	6	6 *
3	54	57
4	99	100
5	86	-82
6	120	-114
7	103	-115
9	53	55
10	82	81
12	94	105
13	76	-91
* H	7	6 *
2	123	120
4	59	61
6	55	-55
10	58	59
* H	8	6 *
1	129	-132
2	102	-96
5	57	60
6	167	163
7	69	-77
8	140	146
9	67	-65
10	58	-68
* H	9	6 *
2	64	-61
4	80	-79
8	79	77
* H	10	6 *
3	100	-102
9	86	-87
* H	11	6 *
6	66	66
* H	12	6 *
1	74	68
1	65	68
2	145	144
4	81	74
5	75	-71
* H	13	6 *
2	78	77
* H	14	6 *
5	58	-64
* H	16	6 *
6	95	97
* H	0	7 *
1	95	-97
3	62	-63
7	73	83
* H	1	7 *
1	352	-344
2	133	137
3	210	-205
5	179	-175
6	74	-75
7	354	-341
8	85	83
9	199	-194
10	77	77
11	74	-76
13	92	-92
15	163	-169
16	61	70
* H	2	7 *
1	85	-85
2	57	63
3	114	115
5	88	83
7	71	-76
9	94	-91
* H	3	7 *
1	170	-170
3	357	-350
4	92	93
5	227	-201
7	205	-200
9	164	-165
10	74	69
11	150	-161
13	78	-84
15	108	-124
* H	4	7 *
1	100	105
5	75	-79
9	57	61
11	57	56
* H	5	7 *
1	209	-207
2	112	-111
3	376	-373
4	59	54
5	221	-216
6	114	114
7	104	-104
9	120	-127
11	200	-217
12	83	82
13	83	-100
* H	6	7 *
3	135	-137
7	61	60
11	86	-89
* H	7	7 *
1	231	-230
3	98	-99
5	183	-176
7	207	-216
8	54	58
9	140	-151
11	105	-126
* H	8	7 *
1	105	-103
5	61	64
* H	9	7 *
2	74	72
3	113	-109
5	203	-203
7	195	-196
8	113	115
9	75	-89
* H	10	7 *
3	64	64
7	91	-98
* H	11	7 *
1	173	-170
3	206	-200
4	59	55
5	109	-110
7	84	-88
9	125	-127
11	88	-94
* H	12	7 *
3	70	-75
5	58	-54
* H	13	7 *
1	134	-133
5	64	-66
9	97	-107
11	93	-97
* H	15	7 *
5	95	-100
7	108	-111
11	63	-66
* H	17	7 *
5	87	-90
7	65	-72
* H	0	8 *
0	211	210
1	88	-87
2	200	195
5	93	94
6	207	203
8	167	158
9	59	-58
10	122	120
11	65	71
14	97	97
* H	1	8 *
2	76	76
4	51	-54
6	67	-71
10	76	77
* H	2	8 *
2	254	255
3	73	-73
4	145	140
6	217	210
7	111	106
8	175	172
10	121	123
13	70	71
14	114	125
* H	3	8 *
2	68	-64
4	69	-68
6	69	74
8	116	118
12	73	-78
* H	4	8 *
1	140	141
2	204	198
4	214	206
5	50	-43
6	124	120
7	55	57
8	69	66
9	73	77
10	133	136
12	87	100
* H	5	8 *
4	76	75
8	70	-74
* H	6	8 *
2	198	194
3	85	88
4	182	175
6	125	134
8	93	100
9	113	119
10	131	149
12	87	123
* H	8	8 *
1	67	-66
2	66	73
4	69	68
5	120	121
6	171	167
8	122	128
* H	9	8 *
2	54	-51
4	84	-87
8	60	65
* H	10	8 *
2	160	161
4	106	109
5	74	72
6	132	130
7	65	67
8	100	104
* H	12	8 *
1	96	101
2	144	143
4	91	94
10	100	99
* H	14	8 *
2	92	81
4	77	79
8	61	62
10	76	78
* H	0	9 *
1	77	-81
3	79	-84
* H	1	9 *
2	96	100
6	75	-78
12	71	-74
* H	2	9 *
1	54	-54
3	100	100
5	80	77
6	51	-47
9	69	-71
* H	3	9 *
8	73	-78
* H	4	9 *
1	82	86
5	81	-83
* H	5	9 *
2	79	-76
6	80	76
8	77	-75
* H	6	9 *
3	67	-65
7	64	76
* H	7	9 *
4	57	-57
* H	8	9 *
1	72	-68
* H	9	9 *
2	57	57
* H	10	9 *
3	83	85
* H	0	10 *
0	116	122
1	89	-86
2	53	56
8	79	79
9	84	-87
* H	1	10 *
2	70	63
6	64	-65
* H	2	10 *
3	65	-58
8	56	64
* H	3	10 *
2	67	-69
8	63	58
12	65	-71
* H	4	10 *
1	53	49
2	70	70
4	88	87
5	92	-94
* H	5	10 *
4	71	79
* H	6	10 *
7	65	-68
* H	8	10 *
1	92	-87
* H	12	10 *
5	70	-69
* H	1	11 *
1	151	-146
3	128	-127
5	124	-126
7	110	-109
11	69	-76
* H	3	11 *
1	157	-154
3	138	-134
5	149	-150
7	90	-99
9	100	-104
11	70	-83
* H	5	11 *
1	129	-131
3	107	-108
5	114	-126
7	93	-91
9	85	-98
* H	7	11 *
1	130	-128
3	113	-116
5	109	-111
7	79	-98
9	67	-83
* H	9	11 *
1	108	-106
3	92	-87
5	80	-78
7	90	-89
9	74	-79
* H	11	11 *
3	95	-93
5	82	-87
9	68	-63
11	65	-54
* H	13	11 *
1	64	-70
* H	0	12 *
0	73	67
4	68	71
* H	2	12 *
4	75	69
* H	8	12 *
2	64	63
* H	2	14 *
4	66	53

[a] First column is *h*, followed by $10F_o$, followed by F_c. F_c(absolute) = F_c(20 × scale factor); scale factor = 0.3239 ± 0.0010.

and cadmium compounds, was first reported to be isostructural, indeed isomorphous, with $Ni(tu)_4Cl_2$,[3] and interpretation of further experimental work has been based on this report.[4,5] A second structure for $Ni(tu)_4Cl_2$ was later reported[6] and showed two significantly different Ni–Cl distances of 2.40 and 2.52 Å, both ±0.02 Å. Preliminary results[7] of the structural determination of $Co(tu)_4Cl_2$ have indicated that the cobalt and iron compounds are indeed isostructural but that the arrangement of ligands and coordination geometry of the $Co(tu)_4Cl_2$ is distinctly different from either of the two structures reported for $Ni(tu)_4Cl_2$. This paper reports the differences found in the X-ray diffraction patterns for the series $M(tu)_4Cl_2$ where M = Mn, Fe, Co, Ni, or Cd, as well as the details and final results of the single-crystal X-ray diffraction study of $Co(tu)_4Cl_2$.

Experimental Section

Crystals of $Co(tu)_4Cl_2$ and $Fe(tu)_4Cl_2$ were prepared by Dr. K. K. Chatterjee and crystals of $Mn(tu)_4Cl_2$ were prepared by Dr. P. Boldrini using the methods described by Nardelli.[8] Crystals of $Ni(tu)_4Cl_2$ and $Cd(tu)_4Cl_2$ were prepared by Nardelli's method[8] but with ethanol instead of water. Crystals of all five complexes were mounted about the fourfold rotation axis and equiinclination Weissenberg photographs were obtained (*hk*0–*hk*2 for $Mn(tu)_4Cl_2$; *hk*0–*hk*3 for $Co(tu)_4Cl_2$, $Fe(tu)_4Cl_2$, $Cd(tu)_4Cl_2$, and $Ni(tu)_4Cl_2$) with Mo Kα radiation. The $M(tu)_4Cl_2$ complexes with M = Mn, Fe, Co, or Cd were found to be isomorphous and have the same cell dimensions as $Co(tu)_4Cl_2$ within the limits of photographic data. These cell dimensions (see below) differ significantly only in the length of the *c* axis [$a = b = 13.524$ (5), $c = 8.981$ (5) Å] from those reported by Truter[6] when the appropriate cell transformation is made. Systematic extinction of 00*l* reflections for $l = 2n + 1$ and of *hk*0 reflections for $h + k = 2n + 1$ indicated the space group $P4_2/n$.[9]

The single crystal of *trans*-dichlorotetrakis(thiourea)cobalt(II), $Co[SC(NH_2)_2]_4Cl_2$, chosen for X-ray data collection measured 0.54 mm × 0.48 mm × 0.53 mm and was mounted with the [110] direction as the rotation axis. The lattice constants were determined by least-squares refinement of the setting angles of 26 reflections that had been carefully centered on a Picker automatic diffractometer. Using Mo Kα radiation (λ 0.71068 Å) the lattice constants at room temperature are $a = 13.508 \pm 0.007$ Å and $c = 9.106 \pm 0.005$ Å. The experimental density of 1.72 g/cm³, measured by flotation in a bromoform–benzene mixture, is within experimental accuracy in exact agreement with the calculated density based on four molecules per unit cell.

The intensities of 885 independent nonzero reflections were recorded by the θ–2θ scan technique using Zr-filtered Mo Kα

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[3] L. Cavalca, M. Nardelli, and A. Braibanti, *Gazz. Chim. Ital.*, **86**, 942 (1956).

[4] F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, **3**, 17 (1964).

[5] D. M. Adams and J. B. Cornell, *J. Chem. Soc., A*, 884 (1967).

[6] A. Lopez-Castro and M. R. Truter, *ibid.*, 1309 (1963).

[7] J. E. O'Connor and E. L. Amma, *Chem. Commun.*, 892 (1968).

[8] M. Nardelli, L. Cavalaca, and A. Briabanti, *Gazz. Chim. Ital.*, **86**, 867 (1956).

[9] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 176.

TABLE IB

UNOBSERVED STRUCTURE FACTORS[a,b]

```
                  F     ≤  F(CALC)  <  2.0·F                (350)
                   MIN                     MIN

L = 0        9 19  60   12 13  62   14  1  47    2 16  43   10  7  50    3  6  47
13  1  66    1 21  48    8 15  45    0  3  42    4 16  49   12  7  54    4  6  43
12  2  40    7 21  55   11 15  54    7  3  48    7 16  40   10  8  47    5  6  47
15  5  72   L = 2       12 15  49   11  3  50   L = 7       11  8  56    6  6  54
16  6  54    7  1  41   15 15  49   13  3  45    4  1  43   12  8  49    2  7  45
 5  7  54   14  1  49   17 15  53    3  4  40   12  1  40   10 10  68    2  8  51
 9  7  40   13  4  46    0 17  52   14  5  53   13  2  50   12 10  65    6  8  58
 3  9  54    3  7  40    1 17  43    4  6  56    2  3  41   13 10  63    7  8  53
 1 11  49    6  7  45    8 17  57   11  7  56    8  3  46    2 11  55    8  8  51
 5 11  41    8  7  41   11 17  51   12  7  42   12  3  56    6 11  51    9  8  42
 9 11  46    1  8  41   15 17  43   13  7  44   15  4  54   10 11  41    4  9  41
14 12  41    3  9  47    5 18  58   11  8  41    0  5  51    0 12  47    8  9  55
 7 13  46    5 10  45    7 19  47    6 10  46   15  5  57    6 12  45    3 10  46
12 14  49    8 10  51    9 19  71   12 11  45   14  7  51    7 12  57    9 10  70
 5 15  45    7 11  47   11 19  47   13 11  71   15  7  45    8 12  52    6 11  41
 8 16  44   14 11  40    1 21  52   14 11  42    6  9  46   12 12  49    2 12  54
 3 17  47   11 12  46    7 21  53   11 13  61    4 10  40    0 13  45    4 12  51
10 18  56   14 12  43   L = 4        4 14  47   11 10  50    2 13  45   10 12  41
12 18  65    4 14  41   11  1  47    5 14  45   15 10  46    6 13  45   L = 11
16 20  43   14 14  49    8  3  48    7 14  68   10 11  44    8 13  54    2  1  61
L = 1       16 14  59    9  3  40    1 15  51   13 11  75    6 14  74    6  1  51
17  1  46    9 15  48   15  3  46    3 15  43   15 11  57    9 14  60    3  2  43
18  1  40    1 16  41    9  4  44    4 15  48    2 13  56   12 14  50    5  2  49
14  2  40    4 16  50    9  5  47   10 15  45    6 13  43   L = 9        7  2  43
18  3  41    8 16  40   13  6  41    3 16  60    7 13  64    7  1  48    9  2  52
12  4  45   12 16  50   15  6  58    4 17  68   12 13  51   10  1  41    0  3  55
13  5  51   14 16  64    5  7  41    7 17  44   15 13  40    7  2  49    4  3  52
10  6  52    0 18  41   10  7  47   13 17  66    1 14  58   10  3  54    1  4  46
12  7  55   12 18  44   10  8  41   L = 6        3 14  44    3  5  50    5  4  55
13  7  52   14 18  40    7 10  40    0  1  46   11 14  61   11  5  49    2  5  54
14  7  43   L = 3       10 10  61    9  1  43    0 15  56    8  6  40    3  6  44
16  7  47   16  1  51   11 10  45   10  1  40    1 15  47   11  6  51    7  6  42
18  7  44   17  3  46   13 10  65   13  2  45    3 15  58    5  8  48    1  8  63
12  8  43   18  3  47   10 11  50    5  3  47    9 15  50    4  9  40    2  9  42
14  9  49    5  4  47   14 11  47    9  3  41   13 15  41    6  9  59    6  9  45
 8 10  58    6  4  41    7 12  41    3  5  42    7 16  48    7  9  49    7 10  50
 5 11  48    8  4  40    9 12  41    5  7  46    0 17  41    7 10  56    7 11  62
10 11  54    4  7  47   10 13  41   12  7  67    1 17  49   11 10  55    3 12  43
12 11  48   10  8  47    1 14  43    1  9  41    3 17  68   L = 10       3 13  64
14 11  58   12  8  40    9 14  70   12  9  40    8 17  55    4  2  62    5 13  71
 6 13  62   14  9  60   12 14  54    2 10  48   13 17  60    6  2  40    7 13  44
 8 13  42    2 10  41    4 15  60    4 11  52   15 17  40    7  2  52    9 13  54
14 13  44    3 10  44    3 16  56   10 11  42   L = 8        9  2  76   L = 12
 5 14  40    4 10  41    5 16  43    3 12  40    5  2  41    4  3  46    0  2  56
10 15  59   11 10  62    6 17  58   11 12  48   12  2  57    9  3  43    2  2  47
13 15  51    0 11  50    8 18  51    4 13  55    9  3  56    0  4  55    1  4  50
14 15  40    6 11  45   10 18  44    6 13  48    0  4  44    6  4  43    2  4  52
15 15  46   16 11  43   11 18  42    8 13  43   12  5  58   10  4  54    0  5  53
17 15  71   18 11  41   14 18  54   10 14  53    1  6  40   11  4  55    2  6  49
 1 17  45   14 12  47    0 19  40   13 14  48    7  6  48    8  5  45    3  6  56
 2 17  44    6 13  63   10 20  70   10 15  41    2  7  41    0  6  50    0  8  55
 6 17  44    7 13  48   L = 5        1 16  65    6  7  43    2  6  42

            2.0·F     ≤  F(CALC)  <  3.0·F                 (23)
                 MIN                     MIN

L = 0       15 11  82   12 10 117    0 20  87   12  9  99   L = 7        4 13  91
10 20 104   17 13  92    2 18 118    2 20 106   13  9  97   13  7  86   L = 11
L = 3        3 19  91    4 18  81   L = 5       11 10  81   13  9 117    9  1 111
17  7  97   L = 4       12 18  79    7  6 100    2 13  86   15  9 104    1 11  81
13 11  95

                    3.0·F     ≤  F(CALC)    (3)
                         MIN

          H  K  L  |F(c)|

          1 19  3   133       14 10  4   193       3 13  7   166
```

[a] First column is H, followed by K, followed by F_c. F_c(absolute) = F_c(20 × scale factor); scale factor = 0.3239 ± 0.0010. [b] For the unobserved reflections there were 1784 for which F_c was less than F(min) for 2θ less than 60°. All reflections not used in the refinement are classed as unobserved, even if they were eliminated because of equipment malfunction.

radiation at room temperature. All independent reflections to $2\theta = 60°$ were measured. The peaks were scanned over a range of 1.5° 2θ for 90 sec and backgrounds were estimated by stationary counting for 40 sec at ±0.75° 2θ of the peak maximum. Integrated intensities were calculated assuming a linear variation in background from the function $I_{\text{net}} = I_{\text{scan}} - 1.125(B_1 + B_2)$, where B_1 and B_2 are the background counts. Reflections were considered absent if the integrated intensity was less than $3 \times 1.125(B_1 + B_2)^{1/2}$. A standard reflection was measured after every ten reflections to ensure stability of the operation. Overall variation of the standard peak throughout the data collection was less than 7% of the total integrated intensity. This change was apparently a combination of two effects, a very slow decrease in intensity with a superimposed slow periodic variation. We believe this to be due to some crystal decomposition as well as to some drift in the electronics. It is not likely due to crystal motion since the centering was carefully checked several times during data collection. Variation from one standard peak to the next was much less than that expected from counting statistics.

The takeoff angle, source to crystal, and crystal to counter values were 3.7°, 18 cm, and 23 cm, respectively, and the receiving aperature at the counter was 6 mm wide × 8 mm high. The half-width at half-peak height for an average reflection was 0.34° at a takeoff angle at 3.7°, indicating that the mosaicity of the crystal was quite small. This is not to be taken as an absolute value of the mosaic spread since this quantity depends upon instrumental factors, but rather only as an indication that the peak was well within the scan interval. The counting rate never exceeded 5000 counts/sec and no attenuators were used.

Twenty general *hkl* reflections were measured in all eight symmetry-related octants and agreed within two standard deviations; otherwise, only the independent reflections in the positive *hkl* octant were scanned. The linear absorption coefficient (μ) for this compound with Mo Kα radiation is 16.7 cm^{-1}, and no corrections were made for absorption. Corrections for Lorentz–polarization effects were made and intensity data were reduced to structure factors. The maximum relative error caused by absorption on intensities would be estimated at 10% of I.

Determination of the Structure

The space group $P4_2/n$ demands that with four molecules of $\mathrm{Co(tu)_4Cl_2}$ per unit cell the cobalt atoms must lie on special positions. The structure was solved by locating the cobalt, chlorine, and sulfur atoms from a three-dimensional Patterson[10] map. Using these atomic coordinates for phase[11] determination, all of the nonhydrogen atoms were located from a three-dimensional electron density calculation. A full-matrix least-squares refinement using isotropic temperature factors resulted in R = 0.071 and weighted R[12] = 0.077. Conversion to anisotropic temperature factors and refinement of all parameters reduced R to 0.051 and wR to 0.064. A three-dimensional difference Fourier map was calculated[10] and all eight hydrogen atoms were clearly resolved. There were no other peaks in the difference map higher than the smallest hydrogen peak, indicating that the hydrogen atoms have been unambiguously located. Using anisotropic temperature factors for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms, a full-matrix least-squares refinement of all parameters resulted in a final R, weighted R, and standard error of an observation of unit weight[12] of 0.045, 0.054, and 1.05, respectively.

The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with unit weights. Scattering factors for neutral nonhydrogen atoms were from Cromer and Waber[13] and those for hydrogen were from Stewart, *et al.*[14] The effects of anomalous dispersion were included in the structure factor calculations by addition to F_c;[15] the values for $\Delta f'$ and $\Delta f''$ for Co, Cl, and S were those given by Cromer.[16] The final tabulation of observed and calculated structure factors is listed in Table IA. Unobserved data were not used in the structure refinement and a listing of those for which F_c exceeds $F_{\min}$ is included in Table IB. Final atomic positional and thermal parameters are listed in Table II.

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(10) Patterson and electron density syntheses were calculated using "ERFR-3, a Three-dimensional Fourier Summation Program Adapted for the IBM 7040 from ERFR-2 of Sly, Shoemaker, Van den Hende," by D. R. Harris, Roswell Park Memorial Institute, Buffalo, N. Y., 1964.

(11) Structure factor calculations and least-squares refinements were performed with a local version of "ORFLS—A Fortran Crystallographic Least-Squares Program," by W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(12) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; weighted $R = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$; standard error = $[\Sigma w(F_o - F_c)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ where NO = 885 and NV = 120.

(13) D. T. Cromer and J. T. Waber, *Acta Cryst.*, **18**, 104 (1965).

(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(15) J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, **17**, 781 (1964).

(16) D. T. Cromer, *ibid.*, **18**, 17 (1965).

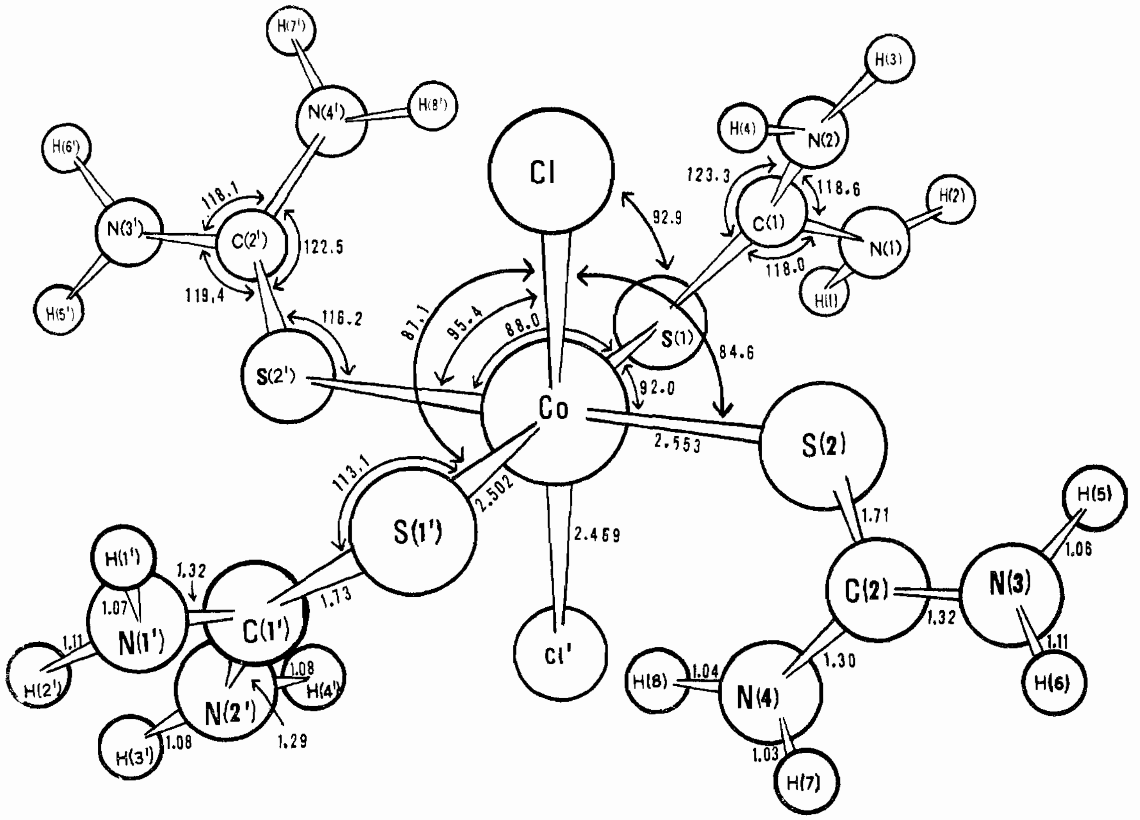

Figure 1.—A perspective view of the molecular configuration of $Co(tu)_4Cl_2$. The cobalt atom lies on a center of symmetry and only independent distances and angles are indicated. Estimated standard deviations are: Co–Cl, ±0.002 Å; Co–S, ±0.006 Å; S–C ±0.013 Å; C–N, ±0.017 Å; N–H, ±0.2 Å; Cl–Co–S and S–Co–S, ±0.1° Co–S–C, ±0.5°; S–C–N, ±1°.

Interatomic distances and angles, root-mean-square components of thermal displacement, dihedral angles between planes, and their errors were computed[17] with the parameters and a variance–covariance matrix from the last cycle of least-squares refinement and are listed on the figures or in Tables III and IV. Least-squares planes for the thiourea groups, including hydrogens, were calculated[18] and are listed in Table III.

Description of the $Co[SC(NH_2)_2]_4Cl_2$ Structure

The structure consists of isolated molecular units of $Co(tu)_4Cl_2$ held together by weak Cl···H–N hydrogen bonds and van der Waals forces (Figures 1 and 2). The cobalt atom is located on a center of symmetry and is coordinated to four sulfur atoms of thiourea groups and to two chlorine atoms in a *trans*-octahedral arrangement of ligands. This requires the two metal to halogen distances to be equal, a marked contrast to the *trans*-$Ni(tu)_4Cl_2$ structure[6] in which the Ni–Cl distances are distinctly different at 2.40 and 2.52 Å, both ±0.02 Å. The two independent cobalt–sulfur bond lengths of 2.502 and 2.553 Å (both ±0.006 Å) are long compared to the expected value of 2.36 Å based on the sum of their covalent radii.[19] A slight lengthening of the Ni–S bond was observed in $Ni(tu)_4Cl_2$ (2.462 ± 0.004 Å *vs.* the expected 2.43 Å).[6] On the other hand, a slight decrease in bond distance is observed both in $Pd(tu)_4Cl_2$ (average Pd–S distance is 2.334 ± 0.003 Å *vs.* the expected 2.36 Å)[20] and in $Pt(tu)_4Cl_2$ (average Pt–S distance is 2.315 ± 0.005 Å *vs.* the expected 2.36 Å).[21] The cobalt–chlorine bond length of 2.469 ± 0.002 Å is also longer than the expected value of 2.31 Å based on the sum of covalent radii.[19] This Co–Cl bond length is approximately halfway between the two Ni–Cl distances observed in the structure reported for $Ni(tu)_4Cl_2$.[6] Interatomic distances within the thiourea groups (Table III) do not differ significantly from each other nor from values reported for other transition metal–thiourea complexes. The average sulfur–carbon and carbon–nitrogen distances of 1.72 and 1.31 Å with individual esd's of 0.013 and 0.016 Å, respectively, also agree well with the values of 1.720 (9) and 1.350 (4) Å reported in the most recent X-ray study of thiourea.[22] The nitrogen–hydrogen distances are all equivalent at 1.1 ± 0.2 Å.

The octahedral configuration around the cobalt atom is slightly distorted from the idealized model with angles of 90°. It can be seen from the L–Co–L′ (where L and L′ are either Cl or S) angles (Figure 1) that three of the

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[17] W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, a Fortran Crystallographic Function and Error Program," Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[18] Program for calculating least-squares planes on the IBM 1620 due to W. A. Spofford, III, University of South Carolina.

[19] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960: (a) pp 246–249; (b) p 260.

[20] D. A. Berta, W. A. Spofford, III, P. Boldrini, and E. L. Amma, to be submitted for publication.

[21] R. L. Girling and E. L. Amma, to be submitted for publication.

[22] M. R. Truter, *Acta Cryst.*, **22**, 556 (1967).

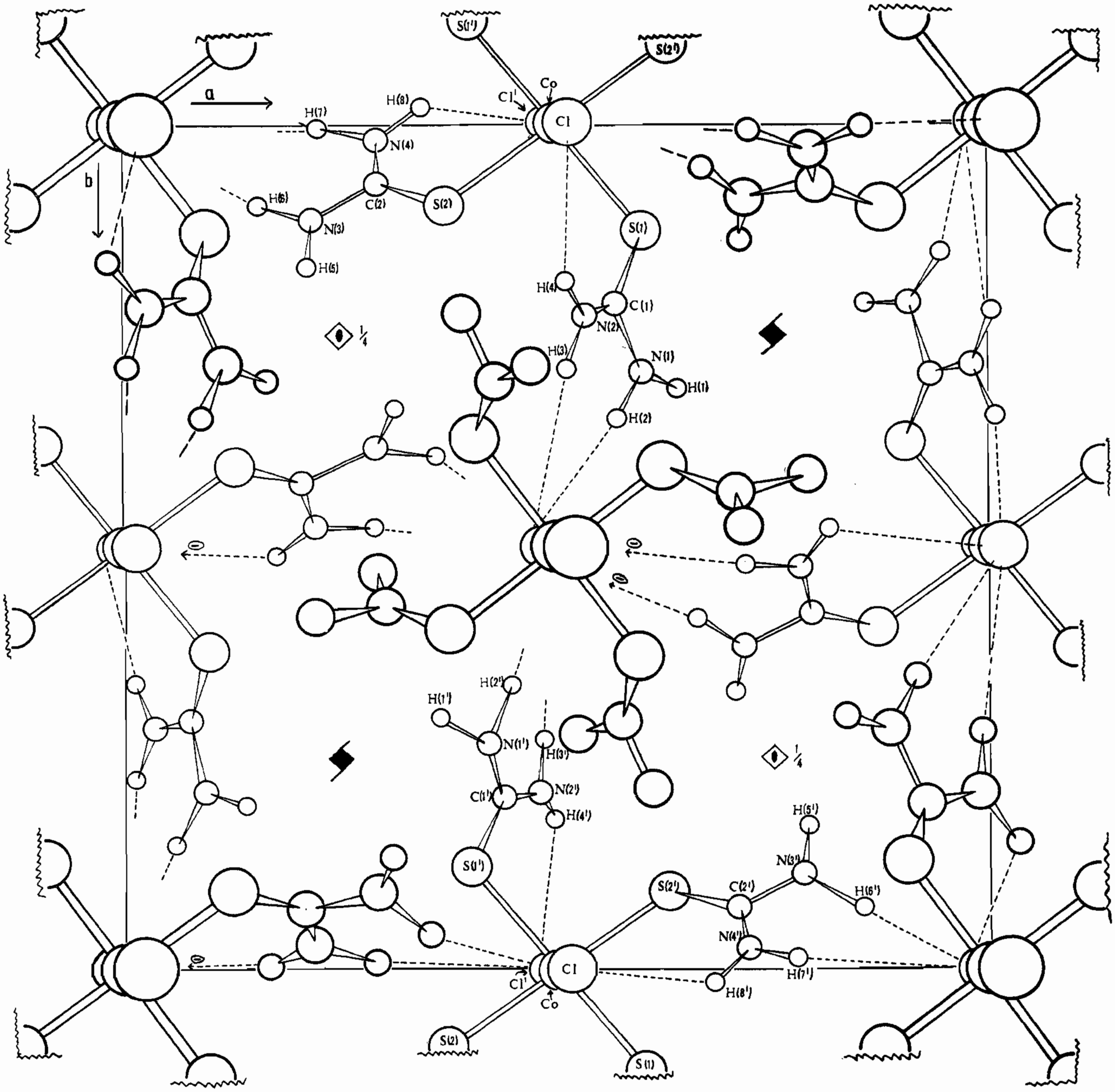

Figure 2.—A perspective view of the molecular packing onto (001). The hydrogen atoms have been omitted from the central molecule for clarity.

six ligands [Cl, S(1′), and S(2)] are distorted toward each other and away from the other three. Owing to the center of symmetry the same is true for the other three ligands [S(1), S(2′), and Cl′)] so that the distortion is in the direction of a trigonal-antiprism configuration. The only reason that can be seen for this distortion in the nonbonded interatomic distances is the relatively short Cl–N(2) distance of 3.24 Å whereas the Cl–S and the other C–N distances are all 3.4 Å or greater. No apparent hydrogen bonding can account for this distortion. This same type of distortion is even more pronounced in the structure of $Ni(tu)_6Br_2$[23] in which three sulfur atoms are displaced toward one another by more than 6°.

The sulfur atoms of the thiourea groups are undoubtedly bonded to cobalt through an sp^2 orbital with its lone pair of electrons. Dihedral angles that completely specify the orientation of the thiourea groups relative to the planes defined by Co and S atoms are listed in Table III. Each thiourea group is slightly tipped (34, 49°) down from the plane defined by Co and the four S atoms. In addition the S(1) thiourea group is twisted about the S(1)–C(1) bond (24°) but the Co, S(2), C(2), N(3), and N(4) atoms are coplanar. This twisting is common in thiourea complexes[6,20,21,23] and the angle is generally between 18 and 26°. Consequently the absence of this twist in the S(2) thiourea group is somewhat unusual. Further, it is interesting to note that

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[23] M. S. Weininger, J. E. O'Connor, and E. L. Amma, *Inorg. Chem.*, **8**, 424 (1969).

TABLE II

FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS AND ESTIMATED STANDARD DEVIATIONS[a]

Atom	x	y	z	Atom	x	y	z
Co	0.5000 (–)[b]	0.0000 (–)[b]	0.0000 (–)[b]	N(4)	0.2532 (9)	0.0100 (8)	−0.1844 (13)
Cl	0.5010 (2)	0.0100 (2)	0.2706 (2)	H(1)	0.656 (13)	0.361 (13)	−0.056 (17)
S(1)	0.6147 (4)	0.1443 (3)	−0.0266 (4)	H(2)	0.566 (11)	0.384 (12)	0.103 (16)
S(2)	0.3491 (3)	0.1131 (4)	0.0184 (3)	H(3)	0.506 (13)	0.309 (13)	0.247 (20)
C(1)	0.5770 (8)	0.2470 (8)	0.0720 (13)	H(4)	0.503 (10)	0.168 (11)	0.222 (15)
C(2)	0.2510 (9)	0.0840 (8)	−0.0923 (12)	H(5)	0.169 (12)	0.186 (13)	0.006 (17)
N(1)	0.6083 (11)	0.3351 (8)	0.0280 (14)	H(6)	0.107 (12)	0.097 (12)	−0.135 (17)
N(2)	0.5197 (9)	0.2420 (10)	0.1853 (13)	H(7)	0.188 (13)	0.009 (13)	−0.241 (20)
N(3)	0.1699 (8)	0.1391 (8)	−0.0873 (13)	H(8)	0.315 (12)	−0.035 (12)	−0.199 (17)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	B, Å^2
Co	21 (2)	25 (2)	56 (2)	−4 (2)	−3 (1)	0 (1)	H(1)	8 (11)
Cl	29 (2)	33 (2)	69 (2)	1 (2)	−4 (2)	1 (2)	H(2)	6 (9)
S(1)	32 (2)	23 (2)	82 (3)	−1 (1)	2 (3)	−5 (3)	H(3)	5 (10)
S(2)	25 (2)	25 (2)	83 (4)	3 (2)	−13 (2)	−8 (2)	H(4)	8 (8)
C(1)	30 (6)	26 (6)	94 (15)	−4 (5)	−17 (8)	4 (7)	H(5)	6 (10)
C(2)	32 (7)	22 (6)	87 (13)	−2 (5)	−9 (7)	11 (7)	H(6)	7 (10)
N(1)	95 (11)	18 (5)	168 (18)	−1 (6)	12 (12)	−8 (8)	H(7)	7 (10)
N(2)	51 (7)	42 (7)	123 (15)	−0 (6)	13 (9)	−29 (8)	H(8)	6 (10)
N(3)	35 (6)	52 (7)	178 (18)	12 (5)	−33 (9)	−32 (10)		
N(4)	41 (7)	39 (6)	91 (13)	−1 (5)	−19 (7)	−14 (7)		

[a] Anisotropic temperature factors are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}kh + 2\beta_{13}hl + 2\beta_{23}kl)] \times 10^4$. Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. [b] Fixed parameter.

the Co–S(2) bond length is significantly longer than the Co–S(1). Whether this lack of twisting of the thiourea group is involved in elongation is difficult to discuss at this time. Part of the reason for this twisting is to be found in the Cl · · · H(4)–N(2) hydrogen bond.

The ability to locate unambiguously all hydrogen atoms not only gives us an opportunity to compare a complexed thiourea ligand with the free thiourea molecule but also gives us the opportunity to observe any hydrogen-bonding effects. Figure 3 shows distances less than 3.0 Å between hydrogen atoms and sulfur and chlorine atoms. The sum of van der Waals radii for H · · · Cl and H · · · S would be 3.00 and 3.05 Å, respectively.[19] It is clearly evident that varying degrees of hydrogen bonding exist in this structure. Each chlorine atom is very close (2.19, 2.20, and 2.22 Å, all ±0.16 Å) to three hydrogen atoms, one within the same $Co(tu)_4Cl_2$ unit as the Cl and two others in adjacent units. Associated with these three H · · · Cl distances are N–H · · · Cl angles of 171, 175, and 167°, all ±8°. At a slightly greater distance from the chlorine atoms are three more hydrogen atoms, one on the same $Co(tu)_4Cl_2$ entity as the Cl (2.59 ± 0.16 Å) and two on adjacent units (2.68 and 2.60 Å, both ±0.15 Å). Associated with each of these H · · · Cl distances are N–H · · · Cl angles of 136, 145, and 147°, all ±8°. Three are eight H · · · S distances ranging from 2.63 to 2.99 ± 0.15 Å that are less than the sum of their van der Waals radii.

We have observed that the visible spectrum of $Co(tu)_4Cl_2$ in anhydrous acetone has the features expected for a tetrahedral Co(II) species. Horrocks[24] has recently shown that $Co(tu)_4Cl_2$ dissociates in acetone solution into $Co(tu)_2Cl_2$ and tu. He has also solved the crystal structure of $Co(tu)_2Cl_2$ and this molecule is, indeed, tetrahedral. Hence, the solution spectrum of $Co(tu)_4Cl_2$ is in reality a measurement of $Co(tu)_2Cl_2$ and not $Co(tu)_4Cl_2$.

TABLE III

SOME H-BONDED DISTANCES[a]

	Distance	Å	Distance	Å
Cl · · · H(4)–N(2)	Cl–N(2)	3.24 (1)	Cl–H(4)	2.19 (16)
Cl · · · H(2)–N(1)	Cl–N(1)	3.49 (1)	Cl–H(2)	2.20 (17)
Cl · · · H(6)–N(3)	Cl–N(3)	3.33 (1)	Cl–H(6)	2.22 (18)
Cl · · · H(8)–N(4)	Cl–N(4)	3.42 (1)	Cl–H(8)	2.59 (18)
Cl · · · H(7)–N(4)	Cl–N(4)	3.58 (1)	Cl–H(7)	2.68 (19)
Cl · · · H(3)–N(2)	Cl–N(2)	3.54 (1)	Cl–H(3)	2.60 (19)

Dihedral Angles (deg) between Normals to Planes Defined by Three Atoms

[S(1)–Co–C(1)] [C(1)–S(1)–N(2)]	24 (1)
[S(2)–Co–C(2)] [C(2)–S(2)–N(3)]	179 (1)
[S(2′)–Co–S(1)] [Co–S(1)–C(1)]	34 (1)
[S(1′)–Co–S(2)] [Co–S(2)–C(2)]	49 (1)

Least-Squares Planes with Equations of the Form $Ax + By + Cz - D = 0$, Where x, y, and z refer to an Internal Orthogonal Coordinate System[b,c]

Eq		Dev from best planes, Å			
		Thiourea Group 1			
A	−0.8015	S(1)	0.0001 (34)	H(1)	−0.03 (12)
B	+0.0872	C(1)	−0.0016 (79)	H(2)	0.11 (11)
C	−0.5916	N(1)	−0.0001 (10)	H(3)	−0.10 (12)
D	−6.3424	N(2)	0.0020 (85)	H(4)	−0.10 (10)
		Thiourea Group 2			
A	+0.3677	S(2)	0.0001 (29)	H(5)	−0.22 (11)
B	+0.5996	C(2)	−0.0057 (78)	H(6)	−0.33 (11)
C	−0.7108	N(3)	0.0050 (80)	H(7)	0.03 (12)
D	+2.5312	N(4)	0.0018 (81)	H(8)	0.03 (11)

[a] All C–N–H angles fall within 2σ of the average 115 (10)°; all H–N–H angles are within 1σ of the average 127 (14°). [b] J. S. Rollett, "Computing Methods in Crystallography," Pergamon Press Inc., New York N. Y., 1965, p 22. [c] Reciprocals of atomic coordinates were used as weights for the respective atoms.

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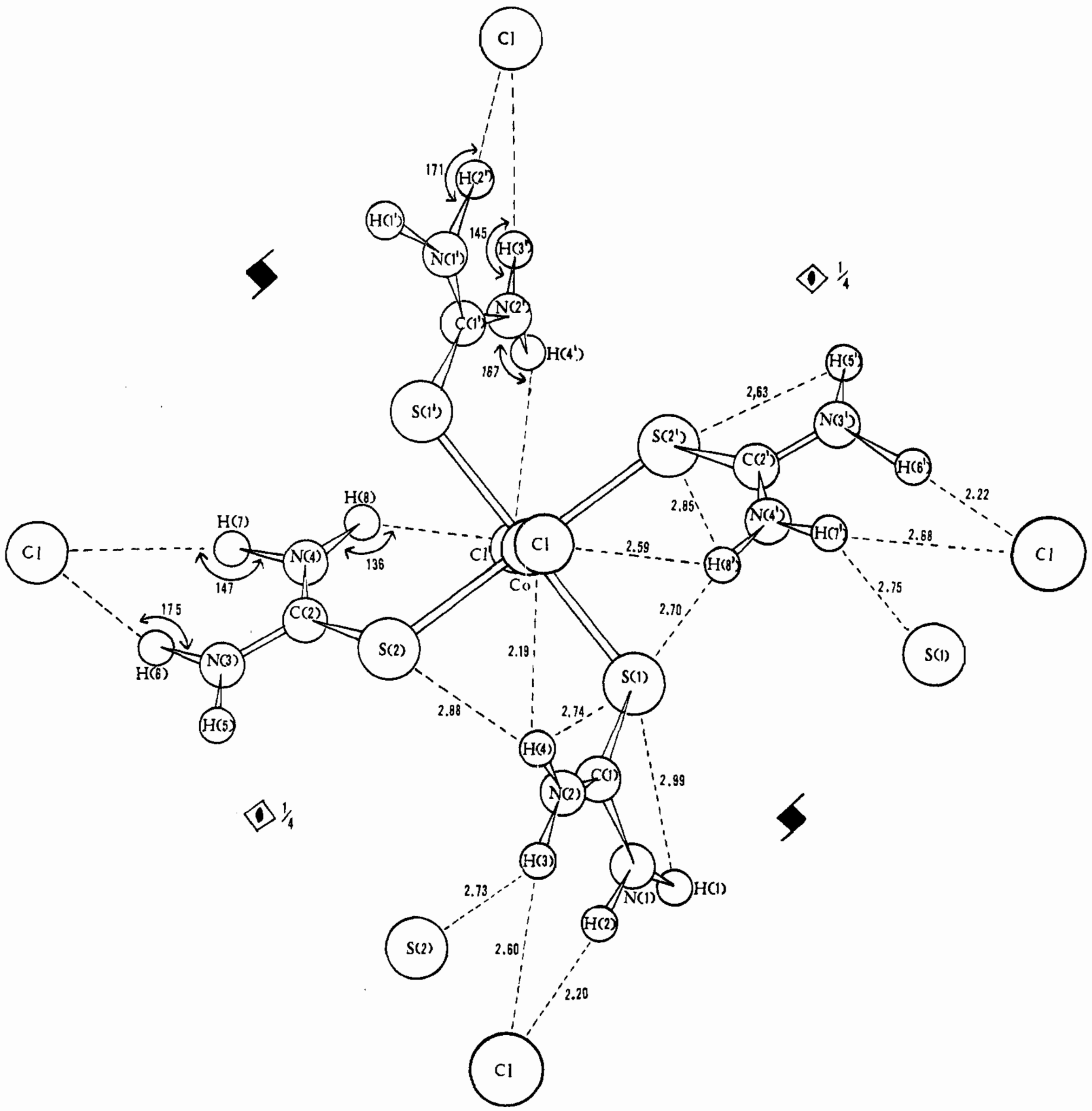

Figure 3.—Hydrogen-bonding scheme in $Co(tu)_4Cl_2$.

TABLE IV

ROOT-MEAN-SQUARE COMPONENT OF THERMAL DISPLACEMENT ALONG THE PRINCIPAL AXES (Å)

Atom	Axis 1	Axis 2	Axis 3
Co	0.129 (9)	0.152 (3)	0.164 (5)
Cl	0.158 (5)	0.176 (5)	0.177 (6)
S(1)	0.145 (6)	0.173 (6)	0.189 (4)
S(2)	0.138 (6)	0.147 (6)	0.205 (5)
C(1)	0.143 (20)	0.157 (20)	0.217 (17)
C(2)	0.134 (20)	0.164 (20)	0.206 (16)
N(1)	0.129 (19)	0.261 (16)	0.302 (17)
N(2)	0.159 (19)	0.215 (16)	0.261 (16)
N(3)	0.153 (18)	0.193 (16)	0.308 (16)
N(4)	0.148 (17)	0.197 (16)	0.229 (16)

Relationship of $Co(tu)_4Cl_2$ to Other $M(tu)_4Cl_2$ Complexes of the Transition Metals

It is germane at this point to discuss briefly why $Co(tu)_4Cl_2$, $Fe(tu)_4Cl_2$, $Mn(tu)_4Cl_2$, $Cd(tu)_4Cl_2$, and $Ni(tu)_4Cl_2$ were thought to be isomorphous. The zero-level Weissenberg photographs (unique axis is the rotation axis) for all five complexes superimpose with one another exactly. However, for the upper level photographs (*hk*1, *hk*2, etc.) there is a distinct difference between the diffraction pattern for $Ni(tu)_4Cl_2$ and the other four complexes. The upper-level diffraction patterns for the cadmium, manganese, iron, and cobalt complexes superimpose exactly but contain additional rows of weak reflections not observed in the pattern for $Ni(tu)_4Cl_2$.

If the $Co(tu)_4Cl_2$ diffraction pattern is indexed conforming to the body-centered cell (I4) of Truter,[6] the additional rows of reflections observed double the *a* and *b* cell dimensions and consequently quadruple the cell volume. The systematic absences are no longer for *hkl*; $h + k = l = 2n + 1$ absent but rather $h + k = 2n + 1$ absent indicating the doubly primitive cell $C4_2/n$. $C4_2/n$ becomes $P4_2/n$ if *a* and *b* axes are chosen 45° to those of $C4_2/n$, of lengths $a\sqrt{2}$ and $b/\sqrt{2}$, yielding a cell having approximately twice the volume of Truter's $Ni(tu)_4Cl_2$ cell. For comparison purposes the diagonal axes of

Truter's cell compared to those of the $P4_2/n$ cell of $Co(tu)_4Cl_2$ are $a = b = 13.524$ (5) Å, $c = 8.981$ (5) Å and $a = b = 13.508$ (7) Å, $c = 9.106$ (5) Å, respectively.

Upon examination of the data for $Co(tu)_4Cl_2$ it was noted that of the 885 observed reflections 499 were consistent with the diffraction pattern for $Ni(tu)_4Cl_2$ (compare with 404 reflections observed for $Ni(tu)_4Cl_2$ by Truter[6]). However, the other 386 reflections that changed the cell represent 43.6% of the total number of reflections but account for only 28.6% of the sum of structure amplitudes. Hence, all five compounds appear to be crystallographically isomorphous if one examines only the *hk*0 Weissenberg photographs and the oscillation photograph rotating about the symmetry axis. However, the symmetry axis is ~0.1 Å longer in the Co type of complex.

The $Co(tu_4)Cl_2$ structure is thus a representative structure for $Mn(tu)_4Cl_2$, $Fe(tu)_4Cl_2$, and $Cd(tu)_4Cl_2$. It is safe to say that these are all *trans* octahedral with both metal–chlorine distances equal in length. On the other hand, *trans*-$Ni(tu)_4Cl_2$ can be viewed as a distortion toward a tetragonal-pyramid configuration. It should be possible with the right combination of sulfur ligands and halogen to form a NiR_4X tetragonal pyramid. It is to be noted that tetrakis(thioacetamide)-nickel(II) chloride is *trans* octahedral with equal Ni–Cl distances at 2.44 ± 0.02 Å[25] and tetrakis(thioacetamide)-nickel(II) bromide is also *trans* octahedral but with a long Ni–Br distance of 3.599 ± 0.004 Å.[26] The structure of tetrakis(dimethylthiourea)nickel(II) bromide is definitely square planar since the bromine is no longer axial and the Ni–Br distance is 4.561 ± 0.003 Å.[27]

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[26] W. A. Spofford, III, and E. L. Amma, to be submitted for publication.

[27] M. S. Weininger and E. L. Amma, to be submitted for publication.

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Complexes of Trivalent Phosphorus Derivatives. XI. Reactions of Cyclopentadienylmanganese Dicarbonyl Nitrosyl Hexafluorophosphate with Various Tertiary Phosphines and Related Ligands[1]

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The manganese salt $[C_5H_5Mn(CO)_2NO][PF_6]$ reacts with various tertiary phosphines and related ligands upon heating in methanol without ultraviolet irradiation to form yellow to orange substitution products $[C_5H_5Mn(CO)(NO)L][PF_6]$ ($L = (C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, and $(C_6H_5)_2PC\equiv CC_6H_5$ but not $(C_6H_5)_3Bi$ or $(C_6H_5O)_3P$). The ditertiary phosphine *cis*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$ reacts with $[C_5H_5Mn(CO)_2NO][PF_6]$ to form the red-orange bidentate monometallic (chelate) derivative $[C_5H_5Mn(NO)(diphos)][PF_6]$. The other ditertiary phosphines $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, *trans*-$(C_6H_5)_2PCH{=}CHP(C_6H_5)_2$, $(C_6H_5)_2PC\equiv CP(C_6H_5)_2$, and $(C_6H_5)_2PCH_2C\equiv CCH_2P(C_6H_5)_2$ may form monodentate monometallic derivatives of the type $[C_5H_5Mn(CO)(NO)(diphos)][PF_6]$ and/or bidentate bimetallic (bridging) derivatives of the type $[C_5H_5Mn(CO)(NO)]_2(diphos)[PF_6]_2$ depending on the ligand and the reaction conditions. The triteriary phosphine $CH_3C[CH_2P(C_6H_5)_2]_3$ reacts with $[C_5H_5Mn(CO)_2NO][PF_6]$ to form $[(C_5H_5)_2Mn_2(CO)(NO)_2(triphos)][PF_6]_2$ in which two of the phosphorus atoms are bonded to one manganese atom and the third phosphorus atom is bonded to the other manganese atom. The infrared and proton nmr spectra of the new compounds are discussed.

Introduction

Within the past few years reactions of a variety of neutral metal carbonyls with numerous tricovalent phosphorus derivatives have been investigated.[4] However, corresponding reactions of metal carbonyl cations with tricovalent phosphorus derivatives have received relatively little attention. A few reactions of $Re(CO)_6^+$ with chelating tertiary phosphines have been reported to give various substitution products.[5] However, no reactions of cyclopentadienylmetal carbonyl cations with tertiary phosphines have been reported although phosphine-substituted derivatives of $C_5H_5Fe(CO)_3^+$ and $C_5H_5M(CO)_4^+$ (M = Mo and W) have been prepared by other methods.[6,7] This paper reports the reactions of the salt $[C_5H_5Mn(CO)_2NO][PF_6]$ with a variety of tertiary phosphines and related ligands. These reactions could be effected thermally in contrast to the corresponding reactions of the isoelectronic $C_5H_5Mn(CO)_3$ with tertiary phosphines which require ultraviolet irradiation.[8]

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