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ıaracterization of the Product Formed by Reaction of 'cloheptatriene with the Strong Inorganic Oxidant s[*cis*-(1,2-perfluoromethylene-1,2-dithiolato)] nickel[1]

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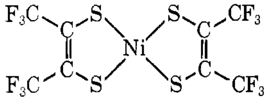
The preparation of $(C_7H_7)[Ni[S_2C_2(CF_3)_2]_2]$ and complete characterization by single-crystal X-ray diffraction and electron paramagnetic resonance studies is described. The material is composed of planar tropylium cations sandwiched between the $S_2C_2(CF_3)_2$(thiete) ligands of alternate square-planar nickel dithiete anions. Each ligand interacts face to face with only one tropylium cation, the result being a sawtooth-like chain structure. The packing implicates the ligand as bearing the anionic charge. The mean plane-to-plane contact is 3.9 Å and the disordered tropylium cations are inclined 17° to the inorganic anion. A three-line powder epr spectrum leads unambiguously to the assignment of the principal g values for $Ni[S_2C_2(CF_3)_2]^-$ as $g_{xx} = 2.137$, $g_{yy} = 2.044$, and $g_{zz} = 1.996$. The crystals studied were monoclinic, belonging to space group $P2_1/n$ with $a_0 = 13.00$ (3) Å, $b_0 = 9.48$ (2) Å, $c_0 = 8.69$ (2) Å, and $\beta = 92.0$ (3)° and containing two formula units per unit cell. The structure was solved using 1221 unique reflections collected by a film method and refined to a final R factor of 13.7% based on F. The inorganic anion is crystallographically required to be centrosymmetric, and the tropylium cation is required to be disordered.

Introduction

Ve have recently characterized the donor–acceptor ıplexes formed by the π accepter bis[*cis*-(1,2 per- ıromethylethene-1,2-dithiolato)]nickel (I^0, nickel di- :te) with the π bases pyrene and perylene.[3]



I^0

:he tendency of I^0 to interact with aromatic mole- :s forming semiconducting molecular solids while :resting in its own right, has led us to speculate on the sibilities of studying organic reactions which might catalyzed or at least promoted by square-planar eptor (or donor) coordination compounds.

'he role of the metal ion in such weakly interacting tems might be similar to that postulated by Mango . Schachtschneider[4] and by Merk and Pettit[5] for :tions going through well-defined organometallic :rmediates. For this reason we are presently study- the effect of I^0 and various other square-planar rdination compounds on forbidden electrocyclic and ıatropic reactions.[6]

Iowever, since I^0 is a very strong oxidizing agent (I^0 e = I^-, +1.0 V *vs.* sce),[7] carbonium ions can be duced and readily so if they possess much electronic ilization energy. Thus we might expect to see a 'rangement, an oxidation, or conceivably an oxida- rearrangement of the organic substrate.

It is the purpose of this report to show that cycloheptatriene undergoes the "equivalent" of a two-electron oxidation in the presence of I^0, to give a tropylium salt of I^-.

Experimental Section

$Ni[S_2C_2(CF_3)_2]_2$ was prepared using the method of Davison, *et al.*[8] Other reagents and solvents, used without purification, were pentane (Matheson Coleman and Bell, practical grade), cycloheptatriene (J. T. Baker, practical grade), benzene (Mallinckrodt, reagent grade), and acetone (solvent grade).

Oxidation of 1,3,5-Cycloheptatriene by Nickel Dithiete.—A 0.5-g (0.98-mmol) sample of $Ni[S_2C_2(CF_3)_2]_2$ was dissolved in 100 ml of pentane, and to this deep violet solution was added a solution of 0.09 g (0.98 mmol) of C_7H_8 in pentane. A green-black precipitate slowly settled. No gas evolution was observed. The precipitate was filtered, washed with pentane, and recrystallized from benzene; yield, 0.27 g (53%), mp 190–191°.

Reaction of Tropylium Tetrafluoroborate with Nickel Dithiete Monoanion.—A 1.0-g (1.96-mmol) sample of $Ni[S_2C_2(CF_3)_2]_2$ was dissolved in acetone to produce the nickel thiete monoanion.[8] Water (60 ml) was added to this solution, followed by 0.45 g (2.5 mmol) of $C_7H_7{}^+BF_4{}^-$ in 15 ml of water. The green-black precipitate was filtered and washed with water. After air drying the precipitate was recrystallized from benzene; yield, 0.8 g (65%); mp 189.5–191°. Products from the two syntheses had identical magnetic properties, *vide infra*.

Magnetic Measurements.—The magnetic susceptibility measurements were made on a variable-temperature Faraday microbalance using $HgCo(CNS)_4$ as a reference.[9] Electron paramagnetic resonance (epr) measurements were made on a Varian V-4502 spectrometer operating at 9.5 GHz using 100-kHz field modulation. The Klystron microwave frequency was measured using a Hewlett-Packard Model 2590A frequency converter and Model 5245L frequency counter. The magnetic field was measured using a proton gaussmeter and the frequency counter described above.

X-Ray Diffraction

A single crystal (0.3 × 0.8 × 0.3 mm) taken from the tropylium oxidation experiments was mounted on its needle axis, [010], in a borosilicate capillary. The cell

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NIH Predoctoral Fellow

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TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (×4.8) IN ELECTRONS FOR $(C_7H_7)[Ni[S_2C_2(CF_3)_2]_2]$

H	L	FOBS	FCAL
****	K=	0	****
0	2	556	506
0	4	74	55
0	6	166	140
0	10	57	50
1	-9	61	33
1	-7	278	281
1	-5	128	152
1	1	61	66
1	3	155	153
1	5	61	46
1	7	56	59
1	9	61	60
2	-8	69	70
2	-6	129	93
2	0	446	557
2	2	67	56
2	4	354	356
2	8	44	26
2	10	75	83
3	-7	229	266
3	-5	107	87
3	-3	150	114
3	-1	445	467
3	1	344	363
3	3	508	617
3	5	200	183
3	7	100	87
3	9	65	52
4	-8	58	35
4	-6	71	63
4	-4	309	353
4	-2	122	104
4	0	496	565
4	2	165	157
4	4	158	142
4	6	19	23
4	8	61	44
4	10	40	26
5	-9	45	51
5	-5	89	68
5	-3	316	316
5	-1	97	78
5	1	68	65
5	3	399	397
5	5	161	154
5	7	83	75
6	-10	42	62
6	-8	48	42
6	-6	49	48
6	-4	272	296
6	-2	201	216
6	0	165	154
6	2	103	103
6	4	60	68
6	6	151	133
6	8	101	95
7	-9	48	59
7	-7	78	71
7	-5	49	29
7	-3	80	53
7	-1	195	176
7	1	174	236
7	3	128	109
7	5	119	116
7	7	138	117
8	-8	46	52
8	-6	61	52
8	-4	56	45
8	-2	53	52
8	0	220	245
8	2	137	134
8	4	136	135
8	6	127	115
8	8	59	69
9	-9	29	34
9	-7	55	71
9	-5	86	87
9	-3	75	68
9	-1	223	217
9	1	197	175
9	3	60	53
9	5	77	65
10	-8	46	50
10	-6	80	92
10	-4	108	97
10	-2	58	53
10	0	197	203
10	2	100	105
10	4	82	52
11	-7	63	60
11	-5	91	108
11	-1	107	79
11	1	74	67
11	3	77	63
11	5	46	19
11	7	70	59
12	-6	39	37
12	-4	55	33
12	-2	81	76
12	0	93	91
12	2	85	70
12	4	139	126
13	-5	72	44
13	-3	82	87
13	1	40	29
13	3	116	101
13	5	[illegible]	[illegible]
14	-4	[illegible]	[illegible]
14	-2	62	67
14	0	60	57
14	2	69	76
14	4	46	37
15	-3	[illegible]	[illegible]
15	-1	47	51
****	K=	1	****
0	1	[illegible]	[illegible]
0	2	266	[illegible]
0	3	49	[illegible]
0	4	69	59
0	5	110	128
0	6	76	94
0	7	[illegible]	[illegible]
0	9	53	42
1	-10	33	19
1	-8	66	48
1	-7	43	41
1	-6	205	192
1	-5	200	204
1	-4	56	34
1	-3	131	114
1	-2	141	107
1	-1	460*	438
1	1	255	265
1	2	145	139
1	3	83	95
1	4	214	214
1	5	99	95
1	6	86	70
1	7	35	30
1	10	65	84
2	-8	95	104
2	-7	201	220
2	-6	70	39
2	-5	112	94
2	-4	69	38
2	-3	107	92
2	-2	95	48
2	-1	275	298
2	0	47	71
2	1	123	88
2	2	205	211
2	3	416	448
2	4	145	142
2	5	159	150
2	6	53	33
2	7	60	42
2	8	98	93
2	9	52	71
2	10	26	31
3	-8	66	54
3	-6	149	154
3	-4	110	98
3	-3	317	311
3	-2	42	40
3	-1	209	216
3	0	40	51
3	1	265	291
3	2	183	185
3	3	164	152
3	4	275	281
3	5	121	96
3	6	88	71
3	7	48	34
3	8	34	19
3	10	53	68
4	-10	29	11
4	-9	39	22
4	-8	56	39
4	-7	81	66
4	-5	113	102
4	-4	83	57
4	-3	381	403
4	-2	159	129
4	-1	27	24
4	0	61	44
4	2	163	176
4	3	391	458
4	4	91	78
4	5	115	171
4	6	54	47
4	8	36	30
4	9	46	48
5	-10	32	33
5	-8	52	38
5	-7	80	74
5	-5	104	103
5	-4	249	291
5	-3	95	83
5	-2	290	310
5	-1	83	97
5	1	70	81
5	2	205	227
5	3	74	70
5	4	167	146
5	5	32	44
5	6	62	59
5	7	44	28
5	8	70	77
6	-9	36	41
6	-8	48	50
6	-7	52	40
6	-6	54	55
6	-5	103	109
6	-4	46	60
6	-3	251	201
6	-2	147	136
6	-1	73	79
6	0	82	71
6	1	90	101
6	2	46	51
6	4	105	115
6	5	26	22
6	7	91	88
6	8	48	40
7	-9	33	30
7	-5	57	44
7	-4	157	165
7	-3	65	52
7	-2	144	135
7	-1	64	62
7	0	182	181
7	1	31	24
7	2	109	80
7	3	73	76
7	4	72	74
7	5	60	55
7	6	149	158
7	7	42	24
7	8	64	76
8	-9	33	30
8	-5	73	83
8	-4	52	24
8	-2	132	137
8	-1	173	175
8	0	47	26
8	1	229	250
8	2	62	46
8	3	72	71
8	4	98	96
8	5	70	66
8	7	88	89
9	-8	36	27
9	-7	43	23
9	-6	65	77
9	-5	67	49
9	-4	46	19
9	-3	78	65
9	-2	68	63
9	-1	89	69
9	0	215	216
9	1	90	87
9	2	47	36
9	3	131	135
9	5	41	33
9	6	64	58
9	7	26	17
10	-7	56	74
10	-5	57	62
10	-4	75	63
10	-3	91	92
10	-2	48	44
10	-1	141	122
10	0	58	48
10	1	90	89
10	5	79	68
10	8	28	33
11	-6	48	69
11	-5	44	31
11	-3	50	35
11	-2	57	43
11	0	52	32
11	1	72	65
11	2	86	90
11	4	123	117
11	5	41	35
12	-7	30	36
12	-5	43	33
12	-4	42	53
12	-3	54	43
12	-1	40	25
12	2	123	117
12	4	62	30
12	5	46	42
12	6	31	32
13	-4	41	53
13	-3	45	36
13	-2	51	61
13	-1	56	52
13	0	62	60
13	1	61	63
13	2	36	50
13	3	38	33
13	4	67	74
13	5	22	13
14	-3	70	83
14	-2	34	25
14	2	40	26
14	3	59	51
15	-4	33	46
15	-2	37	38
15	-1	26	17
****	K=	2	****
0	1	200	221
0	2	57	43
0	4	58	47
0	5	165	149
0	6	158	159
0	7	30	22
0	8	63	42
0	10	42	36
1	-8	80	71
1	-7	105	97
1	-6	182	153
1	-5	115	71
1	-4	71	60
1	-3	52	37
1	-2	629	570
1	-1	799	874
1	0	67	111
1	1	353	428
1	2	349	374
1	3	133	140
1	4	170	140
1	5	258	279
1	6	54	46
1	7	34	20
1	8	76	55
1	9	61	43
2	-9	50	35
2	-8	91	89
2	-6	205	214
2	-5	227	227
2	-4	58	70
2	-3	145	140
2	-2	346	323
2	-1	501	535
2	0	229	321
2	1	130	146
2	2	32	29
2	3	122	80
2	4	106	90
2	5	93	83
2	6	58	47
2	8	30	18
2	9	64	48
3	-9	45	37
3	-8	64	67
3	-7	71	56
3	-6	74	55
3	-4	154	119
3	-3	223	199
3	-2	72	71
3	-1	118	92
3	0	53	52
3	1	217	227
3	2	254	249
3	3	106	104
3	4	123	93
3	5	134	118
3	6	74	58
3	7	50	37
3	8	57	54
3	9	71	74
4	-8	98	113
4	-6	120	108
4	-3	44	34
4	-2	419	457
4	-1	43	39
4	0	55	63
4	1	191	234
4	2	297	312
4	3	47	36
4	4	252	272
4	5	204	193
4	6	30	24
4	7	50	43
4	8	55	61
5	-10	23	19
5	-9	47	57
5	-7	57	51
5	-6	85	67
5	-5	108	112
5	-3	184	191
5	-2	310	340
5	0	155	175
5	1	49	53
5	2	173	162
5	3	119	134
5	4	121	110
5	7	75	56
5	9	22	40
6	-9	45	43
6	-7	59	42
6	-6	71	49
6	-5	143	146
6	-4	167	183
6	-3	75	44
6	-2	53	37
6	-1	74	40
6	0	86	81
6	1	102	108
6	2	221	238
6	4	57	55
6	5	86	81
6	6	113	111
6	7	47	33
6	8	54	58
6	9	32	50
7	-9	39	50
7	-8	53	36
7	-7	51	37
7	-5	120	124
7	-3	151	153
7	-1	42	45
7	0	108	112
7	1	193	220
7	2	121	124
7	3	109	106
7	4	71	68
7	6	53	30
7	7	87	96
7	8	37	41
8	-6	50	58
8	-5	61	28
8	-4	70	69
8	-3	71	60
8	-2	49	23
8	0	187	166
8	1	180	172
8	2	51	37
8	3	94	83
8	4	34	37
8	5	119	127
8	6	88	86
8	7	37	31
9	-7	50	47
9	-6	63	45
9	-5	63	69
9	-4	94	94
9	-2	152	154
9	-1	151	164
9	0	78	65
9	1	174	175
9	4	84	69
9	5	70	72
9	6	33	22
9	7	43	48
10	-8	20	21
10	-6	57	91
10	-5	60	73
10	-4	61	48
10	-3	57	47
10	-2	61	42
10	-1	57	37
10	0	137	129
10	3	81	85
10	4	73	67
10	5	43	34
10	6	70	74
11	-7	32	49
11	-4	71	75
11	-3	53	44
11	-2	48	38
11	-1	93	98
11	3	71	61
11	4	38	16
11	5	66	63
11	6	39	41
12	-7	19	12
12	-6	33	40
12	-3	81	80
12	-1	42	30
12	0	56	41
12	1	96	99
12	2	33	20
12	3	48	30
12	4	60	65
12	5	45	53
13	-6	28	38
13	-3	65	79
13	-2	53	62
13	2	67	65
13	3	70	67
13	4	34	22
14	-5	26	36
14	-4	34	31
14	-2	45	47
14	-1	64	67
14	2	49	41
14	3	31	28
****	K=	3	****
0	1	249	278
0	2	272	229
0	3	157	157
0	4	137	132
0	5	231	247
0	6	83	77
1	-8	58	40
1	-7	93	71
1	-6	179	178
1	-5	95	63
1	-4	85	58
1	-3	138	78
1	-2	355	320
1	-1	257	273
1	0	72	83
1	1	76	71
1	2	44	30
1	3	61	53
1	4	233	216
1	6	133	136
1	9	50	53
2	-8	63	44
2	-6	128	112
2	-5	116	106
2	-4	57	124
2	-2	175	103
2	-1	294	329
2	0	98	126
2	1	96	97
2	2	145	126
2	3	33	23
2	4	147	123
2	5	191	196
2	6	127	109
2	8	50	64
2	9	66	58
3	-10	29	17
3	-9	62	51
3	-8	94	112
3	-7	61	29
3	-6	56	26
3	-5	73	58
3	-4	35	29
3	-3	55	49
3	-2	391	413
3	-1	170	177
3	0	121	128
3	1	73	75
3	2	266	270
3	5	149	145
3	6	69	77
3	7	33	32
3	8	55	73
3	9	72	70
3	10	25	17
4	-9	40	71
4	-7	73	87
4	-6	75	70
4	-5	51	41
4	-3	60	81
4	-2	181	168
4	-1	295	320
4	0	100	82
4	1	147	124
4	2	314	322
4	3	152	124
4	5	38	57
4	6	50	50
4	7	71	68
4	9	69	78
5	-9	45	29
5	-8	76	80
5	-7	56	37
5	-6	52	29
5	-5	148	153
5	-4	41	44
5	-3	192	178
5	-2	67	75
5	-1	295	299
5	0	170	191
5	1	130	131
5	2	191	224
5	8	50	68
5	9	40	24
6	-9	51	78
6	-8	50	34
6	-7	61	61
6	-6	66	66
6	-5	93	90
6	-4	93	97
6	-3	132	127
6	-2	64	67
6	1	234	254
6	2	38	47
6	3	180	158
6	6	47	33
6	7	99	111
6	8	30	32
7	-9	36	43
7	-8	54	42
7	-6	56	63
7	-5	73	64
7	-4	66	82
7	-2	49	36
7	-1	57	44
7	0	158	154
7	1	76	57
7	2	177	187
7	5	152	141
8	-7	48	43
8	-5	125	151
8	-3	99	86
8	-2	138	139
8	-1	32	34
8	1	81	77
8	2	197	190
8	3	39	51
8	4	42	38
8	5	71	71
8	6	50	58
8	7	49	58
8	8	27	33
9	-6	66	84
9	-5	71	51
9	-4	100	109
9	-1	124	106
9	0	113	107
9	1	62	70
9	2	46	30
9	3	39	50
9	4	95	100
9	6	96	96
10	-8	29	29
10	-6	54	49
10	-4	48	40
10	-3	85	94
10	-2	118	115
10	-1	94	89
10	2	61	48
10	3	73	64
10	5	86	82
10	7	23	21
11	-6	44	42
11	-5	65	62
11	-4	47	27
11	-2	113	113
11	-1	50	35
11	0	97	82
11	1	33	25
11	2	77	73
11	4	67	63
11	5	61	62
11	6	34	30
12	-3	50	52
12	-2	77	65
12	-1	74	75
12	2	82	75
12	3	48	39
12	4	42	29
12	5	28	18
12	6	37	43
13	-2	56	62
13	-1	69	67
13	0	55	46
13	1	60	51
13	2	57	51
13	3	39	32
13	4	33	17
13	5	36	33
14	-3	37	33
14	-2	58	61
14	1	51	45
14	2	40	35
14	3	41	35
15	-1	29	22
15	0	26	17
15	2	53	64
****	K=	4	****
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0	2	53	41
0	3	78	57
0	4	202	216
0	5	146	109
0	6	131	159
0	7	39	61
1	-7	59	34
1	-6	83	62
1	-5	210	184
1	-4	240	203
1	-3	222	191
1	-2	170	132
1	-1	212	220
1	0	64	92
1	1	26	22
1	2	145	129
1	3	84	87
1	4	144	127
1	5	237	228
1	6	79	60
1	9	50	20
2	-10	30	34
2	-9	49	54
2	-5	89	66
2	-4	161	133
2	-3	284	251
2	-2	372	397
2	-1	64	34
2	1	97	71
2	2	84	82
2	3	140	131
2	4	210	197
2	5	36	27
2	6	137	121
2	8	52	58
2	9	50	45
3	-9	47	53
3	-7	68	72
3	-6	75	47
3	-5	56	48
3	-4	53	26
3	-3	231	263
3	-2	131	127
3	-1	315	380
3	1	32	22
3	2	146	144
3	3	73	34
3	4	53	28
3	5	66	67
3	6	91	88
3	7	73	101
3	8	42	43
3	9	53	64
4	-8	67	67
4	-7	61	59
4	-6	86	54
4	-4	70	45
4	-3	61	67
4	-2	199	196
4	-1	198	217
4	0	170	162
4	1	91	95
4	2	115	135
4	4	69	66
4	5	67	64
4	6	36	23
4	7	43	28
4	8	81	98
5	-9	46	71
5	-8	58	49
5	-7	71	68
5	-5	68	67
5	-4	150	165
5	-3	175	182
5	-2	98	85
5	-1	126	136
5	0	91	69
5	2	161	164
5	3	125	116
5	4	111	103
5	6	51	35
5	7	78	86
5	9	45	53
6	-8	66	76
6	-6	89	87
6	-5	80	66
6	-4	77	79
6	-3	65	51
6	-2	48	42
6	-1	59	47
6	0	132	135
6	2	234	274
6	3	67	75
6	4	52	53
6	6	46	38
7	-8	40	35
7	-7	45	41
7	-6	46	55
7	-5	112	114
7	-4	62	56
7	-3	43	36
7	-2	88	80
7	-1	93	82
7	0	37	27
7	1	138	141
7	2	98	82
7	3	135	148
7	6	65	67
7	7	31	27
7	8	30	48
8	-6	76	92
8	-4	138	159
8	-3	57	45
8	-1	142	144
8	0	109	118
8	1	43	51
8	2	143	132
8	4	117	116
8	5	68	71
8	6	56	51
8	7	39	30
9	-8	27	31
9	-6	44	27
9	-5	87	92
9	-4	62	42
9	-3	106	111
9	-2	66	56
9	0	38	28
9	2	78	66
9	3	92	90
9	5	92	93
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10	-6	36	28
10	-5	72	68
10	-4	51	56
10	-2	100	102
10	-1	50	50
10	0	63	58
10	1	100	94
10	2	57	68
10	3	72	73
10	4	60	74
10	5	61	76
10	7	21	16
11	-7	25	18
11	-6	38	35
11	-3	60	53
11	-1	116	117
11	2	48	43
11	5	56	52
11	6	31	30
12	-3	34	22
12	-2	76	85
12	-1	55	52
12	0	73	71
12	3	33	38
12	5	54	51
13	-5	31	34
13	-4	39	38
13	-3	20	18
13	-2	38	34
13	-1	73	77
13	1	44	39
13	2	44	42
14	-3	24	11
14	-1	24	21
14	0	44	40
14	1	37	29
14	2	53	62
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0	3	84	129
0	4	119	80
0	5	207	188
0	6	150	131
0	8	59	24
1	-7	59	28
1	-6	62	46
1	-5	111	76
1	-4	257	218
1	-3	119	83
1	-2	234	236
1	-1	150	125
1	0	220	234
1	1	200	203
1	2	73	108
1	3	97	112
1	4	206	191
1	5	60	57
1	6	63	87
1	9	38	28
2	-9	35	39
2	-7	66	54
2	-3	257	171
2	-2	224	141
2	-1	183	168
2	0	77	95
2	2	111	89
2	3	73	70
2	4	114	91
2	5	131	130
2	6	67	72
2	7	76	94
3	-8	45	39
3	-7	71	54
3	-6	64	47
3	-3	215	199
3	-2	283	245
3	-1	219	183
3	0	249	274
3	1	87	67
3	3	78	56
3	4	60	54
3	5	62	76
3	6	77	75
3	8	75	99
4	-9	40	53
4	-8	61	46
4	-7	85	83
4	-6	82	76
4	-4	87	70
4	-3	70	65
4	-2	73	53
4	1	258	284
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5	-3	65	31
5	-2	101	86
5	0	132	108
5	1	159	160
5	2	111	101
5	3	60	65
5	7	60	74
5	8	55	83
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6	-7	71	79
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6	-2	68	63
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7	-6	98	118
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7	-3	113	125
7	-2	53	31
7	-1	158	158
7	1	85	71
7	2	110	118
7	3	40	71
7	4	64	81
8	-5	76	89
8	-4	69	61
8	-3	81	77
8	-2	60	34
8	-1	43	41
8	0	62	56
8	1	60	68
8	3	97	94
8	5	75	85
9	-7	60	53
9	-6	67	39
9	-5	55	62
9	-4	91	97
9	-3	45	37
9	-2	86	85
9	-1	69	72
9	1	111	101
9	2	67	52
9	3	63	69
9	4	99	108
9	6	60	53
9	7	60	55
10	-5	73	81
10	-3	102	95
10	-1	107	97
10	0	56	54
10	4	54	43
10	5	75	86
10	6	36	31
11	-4	67	27
11	-3	63	61
11	-2	72	67
11	-1	65	50
11	0	45	51
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11	4	37	26
11	6	44	47
12	-4	47	53
12	-3	68	45
12	-1	93	103
12	0	68	65
13	-2	40	44
13	0	64	68
13	2	20	20
14	-1	30	30
14	1	36	46
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1	-7	65	40
1	-5	82	70
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1	-2	75	70
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1	2	156	110
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1	4	273	237
1	7	46	68
1	8	66	25
1	9	36	33
2	-6	70	66
2	-5	67	28
2	-4	128	100
2	-3	131	103
2	-2	71	38
2	-1	201	188
2	0	128	128
2	1	203	206
2	2	140	147
2	3	154	136
2	4	154	143
2	5	57	49
2	6	87	69
2	7	50	28
2	8	68	62
3	-8	47	31
3	-6	87	75
3	-5	68	47
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3	3	57	63
3	4	70	56
3	5	51	50
3	7	46	66
3	8	31	32
4	-8	48	52
4	-7	88	79
4	-6	75	89
4	-4	65	50
4	-3	181	169
4	-2	72	68
4	-1	113	113
4	0	184	181
4	2	86	95
4	6	57	72
4	7	86	98
4	8	58	69
5	-8	42	33
5	-7	85	90
5	-6	35	31
5	-5	63	39
5	-4	77	67
5	-3	87	77
5	-2	47	46
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5	1	144	142
5	2	72	67
5	3	106	103
5	4	153	155
5	5	57	70
5	7	42	45
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6	-6	40	40
6	-3	106	104
6	-2	93	87
6	0	108	109
6	1	77	97
6	2	53	91
6	3	106	116
6	7	55	50
7	-7	67	36
7	-6	58	54
7	-5	74	84
7	-4	60	69
7	-3	50	67
7	-2	44	65
7	0	212	207
7	1	95	90
7	3	86	80
7	4	50	63
7	5	56	65
8	-7	53	47
8	-5	43	24
8	-4	80	87
8	-3	105	107
8	-2	102	99
8	2	102	96
8	4	57	74
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9	-4	65	60
9	-3	54	46
9	-1	53	39
9	4	71	82
9	5	50	56
9	6	36	37
10	-6	54	61
10	-2	54	48
10	2	50	66
10	3	73	87
10	4	45	38
10	6	23	26
11	-4	35	46
11	-2	39	79
11	-1	58	63
11	0	109	118
11	1	43	43
11	4	39	46
11	5	22	27
12	-3	52	67
12	-2	44	40
12	-1	32	19
12	0	49	49
12	1	43	33
12	2	31	30
12	3	28	14
13	-1	43	48
13	1	37	39
****	K=	7	****
0	1	121	116
0	2	42	24
0	3	221	217
0	4	68	72
1	-8	59	39
1	-7	71	44
1	-4	122	77
1	-2	96	43
1	1	63	80
1	2	88	90
1	3	220	186
1	5	62	36
1	7	89	71
1	8	64	50
2	-7	57	49
2	-6	73	30
2	-5	130	125
2	-4	166	108
2	-3	84	63
2	-2	65	49
2	0	195	248
2	1	167	182
2	3	204	179
2	4	97	101
2	7	69	44
3	-7	75	58
3	-6	110	100
3	-5	49	45
3	-4	186	167
3	-3	215	164
3	-2	85	53
3	-1	49	31
3	0	119	124
3	2	94	107
3	3	114	102
3	6	54	77
4	-7	81	86
4	-6	97	94
4	-5	96	79
4	-4	129	105
4	-1	68	74
4	0	84	73
4	4	56	61
4	5	58	70
5	-7	66	70
5	-6	72	68
5	-5	80	32
5	-4	93	74
5	-3	58	38
5	-2	99	108
5	-1	77	36
5	0	94	110
5	2	46	59
5	3	96	106
5	4	70	76
5	6	44	96
5	7	56	85
6	-7	41	57
6	-5	65	47
6	-4	35	26
6	-3	102	89
6	-2	69	68
6	-1	168	159
6	0	193	180
6	5	60	92
7	-7	44	13
7	-6	48	18
7	-4	43	50
7	-3	80	87
7	-2	94	109
7	0	47	33
7	1	65	44
7	2	56	52
7	3	88	89
7	4	51	69
7	6	32	47
8	-6	56	49
8	-4	99	109
8	-3	93	100
8	-2	30	26
8	-1	110	110
8	0	30	43
8	3	43	64
8	4	40	45
9	-6	60	61
9	-3	41	37
9	-2	68	65
9	2	54	77
10	-5	41	40
10	0	86	96
10	1	70	86
10	3	45	48
10	6	55	76
11	-6	44	37
11	-3	57	66
11	-1	45	66
11	0	35	37
11	1	45	50
11	2	57	61
11	3	35	53
12	-2	44	31
12	0	41	68
12	1	47	48

constants were determined to be a_0 = 13.00 (3) Å, b_0 = 9.48 (2) Å, c_0 = 8.69 (2) Å, and β = 92.0 (3)° from precession Mo $K\bar{\alpha}$ (λ 0.7107 Å) and Weissenberg Cu $K\bar{\alpha}$ (λ 1.5418 Å) photographs.

Systematic absences for $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) are consistent only with the space group p2₁/n, a nonstandard setting of space group $P2_1/c$ (C_{2h}^5). The small number of reflections of the type $0k0$ made us suspicious of the screw axis, but its presence was later verified in the Patterson synthesis.

The density of the crystal (1.90 (3) g/cm³) indicates two formula units of $C_7H_7[Ni[S_2C_2(CF_3)_2]_2]_2$ per unit cell (Z_{calcd} = 2.02 units/cell).

Reflections were collected for the layers $h0l$ through $h7l$ out to $\sin\theta = 0.95$ on a Nonius integrating Weissenberg camera, using a multiple-film technique. The spots were integrated mechanically during exposure of the films, and the intensities of the expanded spots were measured on a Nonius microdensitometer. Cu $K\bar{\alpha}$ radiation was used and 1221 of the 1706 unique reflections in the sphere of reflection were observed. The intensity data were corrected for Lorentz and polarization effects, and absorption to a cylindrical approximation (μr = 1.7).[10] The data from individual layers

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[10] The programs used in this work were DFSET and GAMP for data reduction and absorption corrections, Busing, Martin, and Levy's ORFLS full-matrix refinement program modified to allow group refinement, Zalkin's FORDAP Fourier summation program, Johnson's ORTEP drawing program, and Wood's MGEOM distance, angle, and plane program.

TABLE II

	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
			Final Parameters[a] for $(C_7H_7)[Ni[S_2C_2(CF_3)_2]_2]$						
Ni	0.0	0.0	0.0	3.8 (1)	0.9 (2)	2.7 (1)	−0.2 (1)	0.2 (1)	0.3 (1)
S_1	−0.1148 (3)	−0.1149 (5)	0.1174 (5)	3.5 (1)	3.6 (3)	4.5 (2)	−0.4 (1)	−0.1 (1)	0.7 (1)
S_2	0.1127 (3)	−0.0460 (5)	0.1774 (5)	4.1 (2)	1.7 (2)	4.6 (2)	−0.6 (1)	−0.3 (1)	1.5 (1)
C_1	−0.054 (1)	−0.180 (2)	0.280 (2)	3.9 (3)					
C_2	0.050 (1)	−0.144 (2)	0.306 (2)	3.6 (3)					
C_3	−0.117 (1)	−0.274 (2)	0.373 (2)	4.5 (3)					
C_4	0.111 (2)	−0.191 (3)	0.445 (2)	5.5 (4)					
F_1	−0.208 (1)	−0.300 (2)	0.318 (1)	9.4 (8)	16.6 (15)	6.7 (7)	−7.0 (9)	1.0 (6)	5.1 (8)
F_2	−0.135 (1)	−0.212 (2)	0.519 (2)	13.9 (11)	7.3 (9)	6.6 (7)	−2.7 (8)	4.0 (7)	1.0 (6)
F_3	−0.077 (2)	−0.393 (2)	0.415 (3)	15.3 (14)	4.5 (9)	23.0 (21)	2.3 (9)	10.5 (15)	8.0 (11)
F_4	0.198 (1)	−0.132 (3)	0.457 (2)	9.7 (10)	19.6 (21)	14.0 (3)	−6.6 (11)	−6.4 (9)	11.9 (14)
F_5	0.070 (1)	−0.173 (3)	0.574 (1)	14.9 (13)	19.4 (19)	4.4 (6)	1.0 (14)	−2.4 (7)	2.7 (9)
F_6	0.137 (2)	−0.326 (2)	0.441 (2)	18.8 (17)	9.5 (13)	9.3 (10)	4.8 (12)	−4.7 (10)	0.5 (9)
			Derived Parameters of Tropylium Group[c]						
T_1	−0.099 (4)	0.396 (6)	0.003 (8)	7.9 (11)					
T_2	−0.101 (4)	0.501 (6)	−0.114 (6)	7.1 (10)					
T_3	−0.027 (3)	0.604 (4)	−0.144 (4)	4.3 (6)					
T_4	0.067 (3)	0.628 (4)	−0.066 (5)	4.0 (5)					
T_5	0.111 (3)	0.557 (5)	0.061 (5)	5.4 (8)					
T_6	0.073 (4)	0.444 (7)	0.143 (6)	6.9 (10)					
T_7	−0.021 (4)	0.371 (4)	0.118 (4)	5.1 (8)					

Standard deviation of last significant figure is in parentheses. [b] Listing of B_{iso} or $B_{ij} = 4b_{ij}/a_i^*a_j^*$, where a_i^* is the ith reciprocal ice vector and the transform of the probability distribution (Tr) = $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + \ldots)$. [c] The group ameters are $x = 0.00$, $y = 0.50$, $z = 0.00$, $\phi = 0.64$ (1), $\theta = 0.661$ (1), and $\rho = 1.59$ (3), where the positions are in fractional co- nates and the angles are in radians.

e scaled individually during refinement, following original adjustment based on $hk0$ precession inten- es.

he atomic-scattering powers of Ni and S were cor- ted for the real and imaginary parts of the anomalous ersion.[11] Scattering powers for Ni^+, F^-, neutral S, C were taken from standard tables.[12]

n the last six cycles of refinement the data were ghted according to the function $w = (1.0 + (F_o/$ $+ (F_o^2/800.0)^{-1}$, and the function minimized was $(|F_o| - |F_c|)^2$.

Determination of Structure

search of the peaks in the Patterson map confirmed presence of the 2_1 axis (*vide supra*) and the choice of /n as the space group. This means that both the n and cation sit on centers of symmetry, and as a sequence the tropylium cation is disordered. The sitions of the two unique sulfur atoms were deter- ned from the same Patterson map.

After the coordinates of the sulfur atoms were im- oved by least-squares refinement, an electron density p was computed. However, while the remaining ms of the inorganic group were readily recognized in is map, and the location of the tropylium ion was parent, its individual atoms were not resolved. herefore, six cycles of refinement of the individual yer scale factors along with nickel thiete atom coor- linates and temperature factors were undertaken, reducing the residue (R) to 0.25.[13] At this point a difference electron density map was computed and the tropylium cation was revealed but still was poorly resolved due to disorder and a large apparent librational amplitude.

TABLE III

DISTANCES[a] (Å) IN $(C_7H_7)[Ni[S_2C_2(CF_3)_2]_2]$[b]

Ni–S_1	2.136 (4)	C_3–F_1	1.29 (2)
Ni–S_2	2.135 (4)	C_3–F_2	1.43 (2)
S_2–C_1	1.71 (2)	C_3–F_3	1.30 (3)
S_2–C_2	1.69 (2)	C_4–F_4	1.27 (3)
C_1–C_2	1.40 (2)	C_4–F_5	1.27 (3)
C_1–C_3	1.46 (3)	C_4–F_6	1.33 (3)
C_2–C_4	1.49 (3)	C–C in tropylium cation	1.4 (1)

[a] Standard deviations in parentheses. [b] Labeling corresponds to that in Figure 1.

The organic cation was placed in the refinement as a D_{7h} rigid group with C–C = 1.40 Å, and six more cycles of refinement, now including the added group positional, rotational, and individual atom temperature factors, reduced the residue to 0.17. The nickel dithiete atoms, except the carbons, were now refined anisotropically to give a residue of 0.137. When the seven tropylium carbon atoms were refined individually, the residue fell to 0.134. Since this is an insignificant improvement[14] and gives no useful information, the constrained model was retained as the final structure. The weighted residue[15] was 0.181 and the standard deviation of an observation of unit weight was 1.80.

The observed and final calculated structure amplitudes are listed in Table I, and the final positional and thermal parameters are given in Table II.

Bond lengths, angles, and best planes are listed in Tables III–V. Standard deviations of these derived

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(11) D. H. Templeton in "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 214, Table 3.3.2.B.

(12) J. A. Ibers, ref 11, p 202, Table 3.3.1.A.

(13) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

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

(15) $R_2 = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

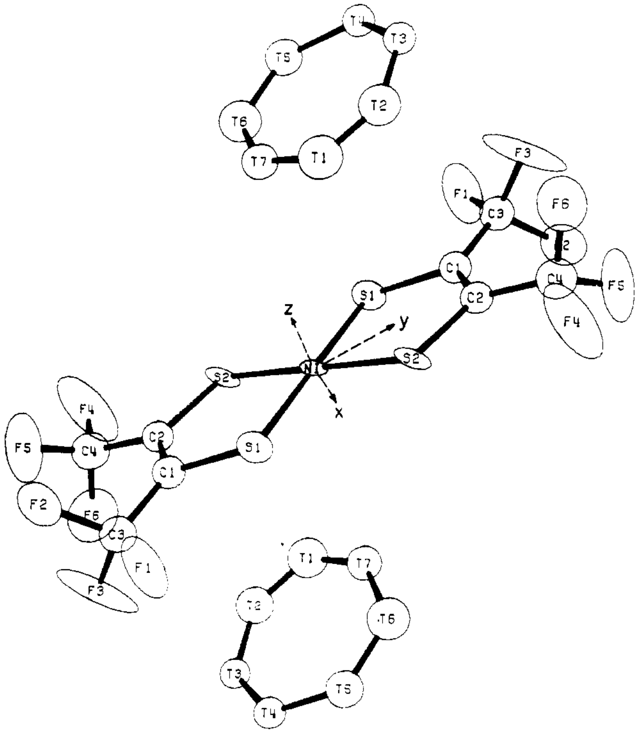

Figure 1.—A perspective view of the $(C_7H_7)[Ni[S_2C_2(CF_3)_2]_2]$ salt showing the environment of the nickel thiete but not the disorder in $C_7H_7^+$. The labeling corresponds to that in the tables. The coordinate system is for reference to the magnetic data.

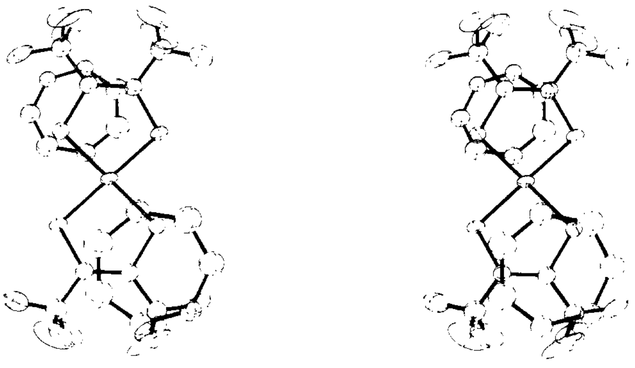

Figure 2.—A view down the normal to $Ni[S_2C_2(CF_3)_2]^-$ showing the interaction between $C_7H_7^+$ and the theite ligands. These drawings constitute a stereopair and may be viewed with a hand viewer.

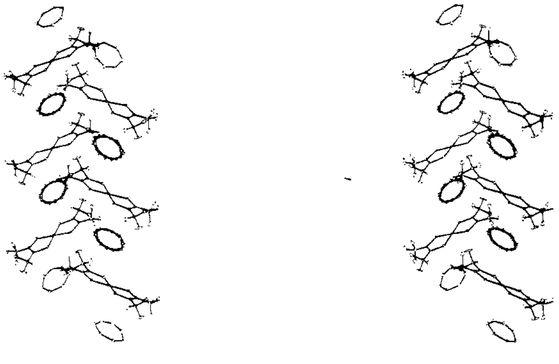

Figure 3.—A section of the $(C_7H_7)[Ni[S_2C_2(CF_3)_2]_2]$ structure showing the chainlike column structure. These drawings constitute a stereopair and may be viewed with a hand viewer.

Table IV

Bond Angles[a] in $(C_7H_7)[Ni(S_2C_2(CF_3)_2]_2$[b]

Angle	Value, deg	Angle	Value, deg
S_1–Ni–S_2	91.4 (1)	C_1–C_3–F_3	117 (2)
Ni–S_1–C_1	105.5 (6)	F_1–C_3–F_2	103 (2)
Ni–S_2–C_2	104.7 (6)	F_1–C_2–F_3	107 (2)
S_1–C_1–C_2	117 (1)	F_2–C_3–F_3	100 (2)
S_2–C_2–C_1	121 (1)	C_2–C_4–F_4	113 (2)
S_1–C_1–C_3	115 (1)	C_2–C_4–F_5	117 (2)
C_2–C_1–C_3	128 (2)	C_2–C_4–F_6	114 (2)
S_2–C_2–C_4	116 (1)	F_4–C_4–F_5	105 (2)
C_1–C_2–C_4	123 (2)	F_4–C_4–F_6	101 (2)
C_1–C_3–F_1	116 (2)	F_5–C_4–F_6	105 (2)
C_1–C_3–F_2	111 (2)		

[a] Standard deviations in parentheses. [b] Labeling corresponds to that in Figure 1.

Table V

Deviations from Best Least-Squares Planes Through Groups of Atoms (Å)

Plane I:[a] $-0.2737x + 0.8204y + 0.5020z + 0.0219 = 0$

Plane II: $-0.2712x + 0.8263y + 0.4935z + 0.0177 = 0$

Plane I						Plane II		
Atom	Wt	Dev	Atom	Wt	Dev	Atom	Wt	Dev
Ni	59	−0.022	T_1	0	3.42	Ni	0	−0.018
S_1	32	0.015	T_2	0	3.72	S_1	32	0.000
S_2	32	0.008	T_3	0	4.13	S_2	32	0.000
C_1	12	0.014	T_4	0	4.34	C_1	12	−0.014
C_2	12	0.038	T_5	0	4.19	C_2	12	0.014
C_3	12	−0.080	T_6	0	3.81	C_3	0	−0.122
C_4	12	0.076	T_7	0	3.46	C_4	0	0.037

[a] The coordinate system is defined by $y \parallel b$ and $z \parallel c^*$.

parameters were estimated using Cruickshank's method.[16]

Discussion

The conclusion that this material is indeed ionic is based primarily on its magnetic properties. First, the bulk susceptibility, which follows the Curie–Weiss law from 77 to 300°K, corresponds to a magnetic moment of 1.81 BM (β). This is to be compared to the value (1.82 β) reported for $[(C_6H_5)_4As]Ni[S_2C_2(CF_3)_2]_2$[8] and the theoretical spin-only value of 1.73 β.

Second, the powder epr consists of three lines which have g values corresponding to a spatial averaging of the principal g values[17] of the nickel dithiete monoanions *via* electron spin exchange between those anions on magnetically inequivalent crystal sites. It is interesting to note here that the relative orientation of the anion pairs which are undergoing the averaging process enables us to make an unambiguous assignment of the principal g values for the nickel dithiete monoanion. These are $g_{xx} = 2.137$, $g_{yy} = 2.044$, and $g_{zz} = 1.996$[17,18] (Figure 1).

Disorder of the tropylium ion prevented meaningful refinement of that group, but there certainly is no indication that it is of other symmetry than planar D_{7h}.

The nickel dithiete monoanion can be compared with

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(16) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).

(17) These are referred to the coordinate system given by R. D. Schmitt and A. H. Maki, *J. Am. Chem. Soc.*, **90**, 2288 (1968). This paper summarizes the magnetic properties of most of the square-planar sulfur complexes of nickel.

(18) A glass (CH_2Cl_2–CHClCHCl) spectrum of the salt gave g values of 1.995, 2.044, and 2.135; the averaged powder spectrum gave g values of 2.017, 2.030, and 2.128.

the neutral nickel dithiete species found in the perylene donor–acceptor molecular solid.[3] The neutral species has an Ni–S distance of 2.122 Å, 0.013 Å shorter than the 2.135 Å for the presently reported monoanion. While expansion of the Ni–S bond upon a one-electron reduction of the nickel complex is consistent both with theoretical predictions[19] and with the existing structural data,[20] it is only on the borderline of being statistically significant.

The perfluoromethyl carbons are very much bent out of the plane of the inorganic anion, seemingly as a consequence of either intramolecular or packing forces, but the large fluorine vibrational amplitudes shown in Figure 1 (mean amplitudes of 0.2–0.8 Å) imply that the CF_3 groups are nearly free rotors. Fluorine amplitudes of about the same size are extant in the structure of the cobalt dithiete dimer[21] but are small in the closely packed perylene–nickel dithiete molecular solid.[3]

The interaction between the organic cation and thiete ligands is illustrated in Figure 2 in which the view is normal to the nickel dithiete anion. The closest contacts (ranging between 3.4 and 4.3 Å, Table V) are between the tropylium ion and the thiete ligands, with the tropylium ion being in effect sandwiched between alternate thiete ligands to form a chainlike structure (Figure 3). The tropylium cations are inclined by 17° to the plane of the nickel dithiete monoanion.

Summary and Conclusions

The ability of nickel dithiete to behave as a strong organic oxidizing agent has been demonstrated by its reaction with cycloheptatriene to form the tropylium salt of nickel dithiete monoanion.

The packing in this ionic compound is loose compared to the neutral donor–acceptor complexes previously studied.[3] This implies that, for the nickel dithiete aromatic complexes, the covalent ground state may be more strongly binding than the excited ionic state.

Acknowledgments.—We wish to thank Professor A. H. Maki for stimulating discussions of nickel dithiete chemistry. Professor Phillip Radlick of this department generously donated samples of cycloheptatriene and tropylium tetrafluoroborate.

The computation center at Riverside, Calif., made available the IBM 360–50 for which we are grateful.

[19] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).

[20] D. Sartain and M. R. Truter, *J. Chem. Soc.*, 1264 (1967).

[21] J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

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Preparation, Structure, and Properties of Bis(N,N-di-*n*-butyldithiocarbamato)gold(III) Bromide and Bis(N,N-di-*n*-butyldithiocarbamato)gold(III) Tetrabromoaurate(III)

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The preparation, electric conductivity, and ultraviolet and infrared spectra of the compounds bis(N,N-di-*n*-butyldithiocarbamato)gold(III) bromide and tetrabromoaurate(III), $[Au(S_2CN(n\text{-}C_4H_9)_2)_2]Br$ and $[Au(S_2CN(n\text{-}C_4H_9)_2)_2][AuBr_4]$, are reported. The crystal structure of the bromide has been determined by a three-dimensional X-ray analysis. This compound crystallizes in the monoclinic space group P2/c. The unit-cell dimensions, measured from photographs, are $a = 11.45 \pm 0.02$ Å, $b = 4.97 \pm 0.01$ Å, $c = 22.62 \pm 0.03$ Å, and $\beta = 97.45 \pm 0.10°$, with two molecules per unit cell. Photometric measurement of equiinclination Weissenberg photographs yielded 1164 intensities. The structural parameters were refined by least-squares methods to a conventional R factor of 0.09. The structure analysis and all reported properties agree with the ionic structure $[Au(S_2CN(n\text{-}C_4H_9)_2)_2]^+Br^-$. The Au(III) is coordinated in planar fashion by four S atoms, the two nonequivalent Au-S distances being 2.309 ± 0.006 and 2.334 ± 0.006 Å. Preparation and properties of the tetrabromoaurate agree with a similar ionic structure $[Au(S_2CN(n\text{-}C_4H_9)_2)_2]^+[AuBr_4]^-$. This complex easily rearranges into the nonionic complex dibromo-N,N-di-*n*-butyldithiocarbamatogold(III). Other reactions and interconversions among $[AuS_2CN(n\text{-}C_4H_9)_2]_2$, $Au(S_2CN(n\text{-}C_4H_9)_2)_3$, $[Au(S_2CN(n\text{-}C_4H_9)_2)_2][AuBr_2]$, $AuBr_2S_2CN(n\text{-}C_4H_9)_2$, $[Au(S_2CN(n\text{-}C_4H_9)_2)_2]Br$, and $[Au(S_2CN(n\text{-}C_4H_9)_2)_2][AuBr_4]$ are described and discussed. Remarkable shifts of the C–N stretching frequency in the infrared spectra of the bromide and the tetrabromoaurate as compared with that of the analogous dibromoaurate[1] are explained in terms of the crystallographic positions of the anions near the nitrogen atom of the cation.

Introduction

Recently the structure and properties of the compounds $[Au(dtc)_2][AuBr_2]$[1] and $AuBr_2(dtc)$[2] (dtc = N,N-di-*n*-butyldithiocarbamate = $S_2CN(n\text{-}C_4H_9)_2$) were reported. The structure of the former was proved to be $[Au(dtc)_2]^+[AuBr_2]^-$ with Au(III)- and Au(I)-containing complex ions, respectively. We have now prepared the new complexes $[Au(dtc)_2]Br$ and $[Au(dtc)_2][AuBr_4]$. The preparations and electrical conductivity measurements reveal these structures to be ionic also, with the same cation, $Au(dtc)_2^+$. However,

[1] P. T. Beurskens, H. J. A. Blaauw, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, **7**, 805 (1968).

[2] P. T. Beurskens, J. A. Cras, and J. J. Steggerda, *ibid.*, **7**, 810 (1968).