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THE STRUCTURE OF THE NICKEL BIS(1,2-ETHENEDITHIOLATE)/2,3-DIMETHYLBUTADIENE CYCLOADDITION REACTION PRODUCT

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SUMMARY

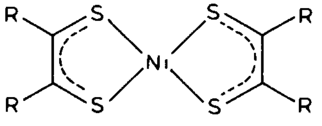
The synthesis and chemistry of the cycloaddition products formed by reaction of various dienes with nickel bis(1,2-ethenedithiolate) is reported.

An orbital correlation model previously proposed in describing these and the related olefin reactions is supported by an X-ray diffraction study of the 2,3-dimethylbutadiene/nickel bis(1,2-ethenedithiolate) structure. This study confirms that the products formed by olefins and dienes are close structural relatives.

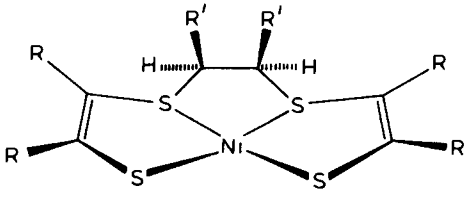
Briefly the structures show a tetradentate sulfur ligand coordinated to square planar nickel. The central ring of the three chelate ring structure is formed in the cycloaddition reaction, and in the present case of a seven membered ring is completely strain free. Bond lengths and molecular properties suggest that reaction is redox in nature with nickel bis(1,2-ethenedithiolate) being the oxidant or acceptor molecule. The crystals studied were monoclinic $P2_1/c$ with $a=7.393(9)$, $b=13.624(21)$, $c=20.003(26)$Å and $\beta=90.80(5)°$. The unit cell contains 4 formula units and the structure was solved using 1333 diffractometer measured intensities and refined to a final R factor of 0.094 based on F.

INTRODUCTION

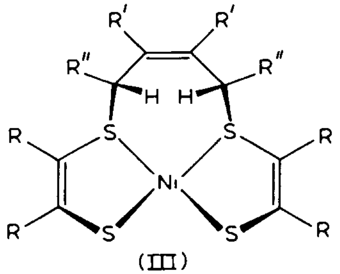
Reactions[1,2] of nickel bis(1,2-ethenedithiolates), (I), with olefins give the cycloaddition products (II), which dissociate upon irradiation in the visible-ultraviolet region to give free olefin and (I). Conjugated olefins react much more rapidly to give related products (III). Furthermore, (III) is found to be in thermal equilibrium



(I)



(II)



(III)

R = CF_3, C_5H_6
R' = Alkyl, H
R'' = Alkyl, H

with (I) and free olefin. Thus we were led to propose an orbital correlation model which serves as a classification scheme for these reactions[3]. (Fig. 1).

Pivotal to this scheme, of course, is the structural relationship between products II and III. Since a structure proof has not been possible by spectroscopic or chemical means we would like to present the results of a single crystal X-ray diffraction study which shows the structures to be those given in Fig. 1.

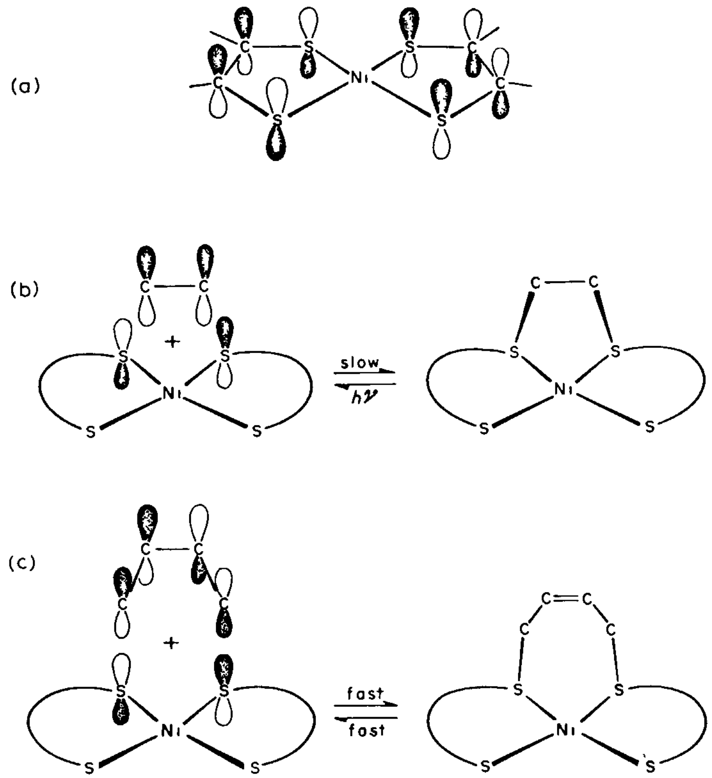


Fig 1 An orbital correlation for the reaction of olefins with nickel bis(1,2-ethenedithiolate).
(a) Lowest lying unoccupied orbital (b_{2g})
(b) Correlation of orbital (a) above with the highest occupied orbital of ethylene to show that the reaction is orbitally forbidden
(c). The same correlation, but with butadiene showing the reactions to be orbitally allowed

EXPERIMENTAL

Yellow-green prismatic crystals of the 2,3-dimethylbutadiene/nickel bis[1,2-bis(trifluoromethyl)-1,2-ethenedithiolate adduct, (III), were grown by slow diffusion of nickel bis[1,2-bis(trifluoromethyl)-1,2-ethenedithiolate (100 mg; 0.196 mmol. in 50 ml hexane) into a CCl_4 solution of the olefin (1 gm; 12.2 mmol in 5 ml), M.p. 153–154° dec. Found: C, 28.31; H, 1.71. $C_{14}H_{10}F_{12}S_4Ni$ calcd.: C, 28.35; H, 1.70%.) A well-formed needle 0.1 × 0.7 × 0.1 mm *a*/*b*/*c* was selected for the X-ray work.

Precession (Mo-K_α) and Weissenberg (Cu-K_α) photographs indicated that the crystal was monoclinic and the space group $P2_1/c$ is uniquely determined by the systematic absences for $0k0$, $k \neq 2n$; $h0l$, $l \neq 2n$. The unit cell constants $a = 7.393(9)$, $b = 13.624(21)$, $c = 20.003(26)$Å and $\beta = 90.80(5)°$ were determined from a least squares fit of 12 carefully centered reflections having $2\theta > 20°$ using Mo-K_α, radiation ($\lambda = 0.70926$Å). The density observed by flotation, 1.93 gm/ml, is in acceptable agreement with the 1.96 gm/ml calculated for 4 formula units per cell.

Reflection data were collected under computer control using a Picker FACS II four-circle diffractometer with a crystal to scintillation detector distance of 320 cm and pulse height analyzer set to accept 90% of a reflections intensity. The moving crystal-moving counter technique was used and the 2θ scan rate was 1°/min. The 2θ scan range was $(1.5 + \Delta)$ where Δ is included to account for the variation in 2θ separation of α_1 and α_2 peaks and the 10 sec background counts taken at the lower and upper limits were averaged to give the background. Mo-K_α radiation made monochromatic by Bragg reflection from a graphite crystal was used in collecting the 1333 unique intensities, of a possible 1970 in the limiting sphere $\sin\theta/\lambda = 0.48$ Å^{-1}, which were 3σ above background.

The data were corrected for Lorentz and polarization effects but not for absorption, since the linear absorption coefficient was small (14.8 cm^{-1}). Three standards, remeasured every 50 reflections, showed only small statistical fluctuation during the data collection.

The structure was readily solved by heavy atom methods* and full matrix least squares refinement with all atoms but carbon allowed to vibrate anisotropically converged to final weighted** and unweighted*** residues (based on F) of 0.094 and 0.095 respectively. The standard deviation of an observation of unit weight is 1.49. Observed and final calculated structure factors**** are given in Table 1, and positional and thermal parameters are listed in Table 2. Structural parameters derived from the X-ray data are presented in Tables 3–5.

(*continued on p* 446)

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* The programs used were local modifications of Eiss' REDAT for data reduction, Zalkin's FORDAP for Patterson and electron density maps, Busing, Levy, and Martin's ORFLS for least squares refinement, Johnson's ORTEP for drawings and Rao's and Lin's GEOM for distances, angles and planes

** $\omega\ R = [\omega(|F_o| - |F_c|)^2/\omega\ F_o^2]^{\frac{1}{2}}$ where $\omega = 4F_o^2/L^2\ \sigma(I)$, L being the reciprocal Lorentz-polarization correction, and $\sigma(I) = [P + (t/20)^2\ B + (0\ 045I)^2]^{\frac{1}{2}}$

*** $R = ||F_o| - |F_c||/|F_o|$

**** The atomic scattering power of Ni was corrected for the real and imaginary part of the anomalous dispersion see ref 4 Scattering powers for Ni^+, F^-, and neutral S,N,C, and H were taken from ref. 5

TABLE 1

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (× 2.4) IN ELECTRONS FOR NICKEL BIS(1,2-ETHENEDITHIOLATE/2,3-DIMETHYLBUTADIENE

K	L	FOBS	FCAL
****	H=	0	****
0	2	70	245
0	4	139	140
0	6	184	179
0	8	175	171
	10	257	258
0	12	[illegible]	91
0	13	77	0
0	14	105	103
0	16	36	5
0	18	93	92
1	2	40	104
1	3	211	210
1	4	245	267
1	5	57	60
1	6	119	[illegible]
1	7	29	26
1	9	244	257
1	10	135	130
1	11	107	107
1	12	205	212
1	13	70	85
1	14	116	123
1	15	100	89
1	16	35	24
1	18	45	55
1	19	38	18
2	0	86	61
2	1	126	111
2	2	283	269
2	3	606	610
2	6	173	170
2	7	83	72
2	9	37	33
2	10	85	86
2	11	268	276
2	12	183	172
2	13	106	99
2	14	149	143
2	15	38	10
2	19	43	35
3	1	160	183
3	2	29	34
3	3	65	64
3	4	117	132
3	5	235	220
3	6	64	55
3	7	152	151
3	8	109	120
3	9	58	46
3	10	83	87
3	11	84	65
3	12	131	124
3	13	70	74
3	16	97	99
3	18	36	24
4	0	239	236
4	2	124	131
4	3	258	238
4	4	159	150
4	9	41	37
4	10	38	32
4	11	85	82
4	13	128	120
4	14	37	35
4	18	78	74
5	3	57	67
5	4	60	66
5	9	69	76
5	10	117	122
5	11	159	163
5	12	161	169
5	13	64	52
10	10	42	19
11	2	39	51
11	5	74	74
11	7	74	79
11	8	56	59
11	9	58	7
12	0	48	41
12	1	42	12
12	5	36	23
12	6	38	22
12	7	59	49
13	2	36	5
****	H=	1	****
0	0	799	743
0	2	172	159
0	-2	195	187
0	4	157	159
0	-4	243	256
0	6	136	151
0	8	128	135
0	-8	667	665
0	10	151	151
0	-10	532	513
0	12	74	94
0	14	130	121
0	16	39	32
0	-16	76	77
0	-18	175	170
1	0	101	90
1	-1	133	113
1	1	72	48
1	2	61	87
1	-3	202	202
1	3	118	121
1	-4	129	124
1	4	224	223
1	-5	119	112
1	5	50	38
1	-6	149	147
1	-7	93	98
1	7	45	20
1	8	53	53
1	-9	372	377
1	9	41	31
1	-10	75	74
1	10	121	125
1	-11	76	68
1	11	77	73
1	-12	201	206
1	12	118	116
1	-13	41	36
1	13	125	115
1	-14	141	129
1	14	72	73
1	15	47	37
1	-17	67	69
1	17	42	30
1	18	48	35
2	0	174	161
2	1	143	168
2	-1	46	33
2	2	421	473
2	-2	39	58
2	3	752	819
2	-3	64	101
2	4	768	406
2	-4	142	133
2	5	110	107
2	-5	91	83
2	6	213	223
2	-6	246	134
2	7	33	51
2	-7	319	312
4	16	56	47
4	-16	39	51
4	-17	77	84
4	18	85	74
5	0	200	187
5	-1	51	38
5	1	236	237
5	2	199	181
5	-3	89	93
5	3	244	238
5	-4	65	52
5	4	407	400
5	-5	30	12
5	5	171	174
5	-6	45	39
5	6	57	48
5	8	47	30
5	-9	58	53
5	9	123	118
5	-10	108	99
5	10	151	241
5	-11	35	35
5	11	164	152
5	-12	45	19
5	12	150	136
5	-13	132	134
5	13	68	57
5	-14	41	44
5	14	71	76
5	15	95	76
6	0	164	174
6	1	98	108
6	-1	262	286
6	2	52	44
6	-2	278	304
6	-3	201	214
6	4	35	34
6	-4	105	103
6	5	59	48
6	-5	91	96
6	6	61	62
6	-6	81	81
6	7	118	125
6	-7	147	158
6	8	64	60
6	-8	162	176
6	9	88	102
6	10	58	51
6	-10	58	66
6	11	88	93
6	-11	49	53
6	12	138	138
6	-12	67	68
6	13	110	105
6	14	36	10
6	-14	37	37
6	-15	58	60
6	16	56	55
6	-16	39	54
6	-17	32	50
7	0	138	140
7	-1	111	113
7	1	229	231
7	-2	248	233
7	2	60	63
7	-3	210	216
7	3	30	17
7	-4	70	64
7	4	98	91
7	-5	39	45
7	6	50	33
7	-7	162	157
7	7	220	217
10	7	89	74
10	-7	86	96
10	8	99	101
10	-9	44	31
10	10	40	39
10	-11	36	30
11	-1	59	56
11	2	51	57
11	-3	69	71
11	3	52	54
11	-4	56	66
11	5	54	31
11	6	76	85
11	7	138	132
11	-8	41	33
11	8	42	38
11	-9	73	73
11	9	62	60
11	-10	39	29
11	10	55	46
12	1	52	45
12	-3	49	49
12	4	36	7
12	-4	49	46
12	5	57	50
12	-6	46	37
12	7	40	13
13	0	40	29
****	H=	2	****
0	0	68	79
0	-2	128	125
0	2	80	74
0	-4	211	211
0	4	205	200
0	-6	149	147
0	6	34	8
0	-8	302	313
0	8	173	180
0	-9	31	0
0	-10	289	299
0	11	36	0
0	-12	94	93
0	12	35	23
0	-13	42	0
0	14	106	111
0	-16	116	123
0	-18	144	165
1	0	134	119
1	1	145	167
1	-1	31	25
1	2	472	467
1	-2	395	374
1	3	161	154
1	-3	162	139
1	4	145	144
1	-4	57	55
1	5	43	65
1	-5	49	51
1	6	33	38
1	-6	138	151
1	-7	109	124
1	8	30	33
1	-8	61	47
1	9	70	66
1	10	65	81
1	-11	34	46
1	-12	74	67
1	13	47	33
1	-13	70	77
1	-15	53	58
1	-16	42	36
1	-17	93	98
2	0	131	115
4	3	263	241
4	-4	343	331
4	4	202	192
4	-5	280	259
4	5	148	143
4	-6	81	69
4	6	124	129
4	-7	58	49
4	7	254	241
4	-8	89	92
4	8	154	158
4	-9	60	64
4	9	77	81
4	-10	228	233
4	10	106	86
4	-11	114	102
4	11	39	44
4	13	45	34
4	14	252	236
4	-15	61	73
4	16	96	77
4	-17	66	63
5	0	248	258
5	1	360	368
5	-1	111	114
5	2	204	211
5	-2	149	149
5	3	175	174
5	-3	76	70
5	4	142	141
5	-4	218	234
5	5	105	118
5	-5	97	109
5	6	77	86
5	-6	118	120
5	-7	146	150
5	8	53	72
5	-8	45	49
5	9	87	90
5	10	141	148
5	11	42	53
5	-11	113	116
5	12	145	133
5	-12	52	54
5	13	66	65
5	-14	79	82
5	-15	43	39
5	16	44	15
6	0	101	96
6	-1	155	149
6	1	43	21
6	-2	98	96
6	-3	51	44
6	3	36	28
6	-4	87	79
6	4	88	91
6	-5	85	84
6	5	74	74
6	-6	141	140
6	6	165	151
6	-7	158	154
6	-8	65	78
6	8	46	43
6	-9	46	51
6	9	51	31
6	-10	109	102
6	10	38	39
6	-11	179	170
6	11	107	111
6	-12	130	131
6	12	133	128
6	-13	71	72
6	13	73	74
10	4	42	26
10	5	39	40
10	-6	87	89
10	6	114	102
10	-7	54	45
10	7	102	90
10	8	123	104
10	9	41	41
10	11	44	33
11	0	92	101
11	-1	116	131
11	-2	47	49
11	-3	180	181
11	4	54	39
11	-4	116	130
11	5	73	89
11	-5	74	82
11	6	64	58
11	7	113	119
11	-7	62	53
11	8	36	32
11	9	57	52
12	1	63	52
12	-2	41	18
12	2	47	44
12	-3	92	91
12	3	39	33
12	4	45	46
12	-5	67	62
12	5	56	43
****	H=	3	****
0	0	40	39
0	2	161	159
0	-2	33	34
0	4	265	274
0	-4	35	29
0	6	92	88
0	8	62	60
0	-8	131	127
0	10	34	16
0	-10	51	58
0	12	45	48
0	-12	99	85
0	14	96	101
0	-14	41	41
0	-16	105	110
1	0	83	82
1	-2	30	17
1	2	44	40
1	-3	114	103
1	3	58	60
1	-4	75	71
1	4	52	54
1	-5	72	76
1	5	86	91
1	-6	274	281
1	6	82	77
1	-7	32	22
1	7	103	92
1	-8	156	129
1	8	40	29
1	-9	42	28
1	9	52	39
1	10	42	20
1	-11	65	50
1	11	153	142
1	-12	78	87
1	12	48	44
1	-13	79	92
1	-14	67	40
1	-15	41	29
1	15	67	49
1	-16	91	92
4	5	180	185
4	-5	177	178
4	6	322	340
4	-6	63	46
4	7	118	119
4	-7	203	199
4	-8	210	207
4	9	58	57
4	-9	102	92
4	10	38	43
4	-10	51	37
4	-12	62	60
4	-13	48	49
4	14	139	151
4	-14	88	86
4	-15	61	55
4	16	55	62
4	-16	47	37
5	0	229	213
5	-1	109	94
5	1	62	52
5	-2	34	40
5	2	130	125
5	-3	57	39
5	-4	267	247
5	4	84	84
5	-5	76	72
5	-6	286	273
5	-7	96	87
5	7	100	74
5	-8	222	207
5	8	156	132
5	-9	170	158
5	9	68	43
5	-10	40	6
5	10	113	107
5	11	46	51
5	-12	59	58
5	12	67	55
5	-13	47	32
5	13	47	53
5	-14	67	64
5	-15	56	61
5	15	66	46
5	-16	43	56
6	0	86	93
6	1	38	35
6	-1	48	51
6	2	35	33
6	-2	172	179
6	3	151	158
6	-3	120	121
6	4	149	159
6	-4	74	64
6	5	72	80
6	-5	105	100
6	6	88	95
6	7	124	136
6	8	130	141
6	-8	48	56
6	9	106	118
6	-9	41	58
6	10	70	80
6	11	43	39
6	-12	87	89
6	-13	62	58
6	-14	42	35
6	15	52	36
6	-15	84	82
7	0	38	34
7	-1	63	61
7	1	46	36
7	-2	128	117
0	6	167	157
0	8	59	67
0	-10	128	140
0	10	73	59
0	-12	156	163
0	14	43	33
0	-16	58	51
1	0	40	36
1	-1	48	39
1	3	111	101
1	-3	63	58
1	4	105	115
1	-4	67	57
1	5	96	99
1	-5	91	87
1	6	51	55
1	-6	96	91
1	7	133	151
1	-7	100	100
1	8	206	236
1	9	124	135
1	-9	135	143
1	10	94	102
1	-12	81	98
1	-14	98	100
1	-16	76	72
2	0	143	134
2	1	94	119
2	-2	44	30
2	2	187	183
2	-3	37	20
2	3	126	127
2	-4	56	52
2	4	120	116
2	-5	232	223
2	5	92	96
2	-6	93	86
2	-7	85	75
2	7	183	179
2	-8	61	48
2	8	94	84
2	-9	41	22
2	9	88	67
2	-10	74	69
2	-11	48	60
2	11	38	12
2	12	39	34
2	13	82	91
2	-14	65	68
2	-15	137	147
2	15	45	33
3	0	57	58
3	-1	176	169
3	2	68	88
3	-2	94	90
3	3	160	171
3	-3	400	367
3	4	149	161
3	5	133	128
3	-5	223	208
3	6	91	98
3	-6	244	232
3	7	74	78
3	-7	72	64
3	8	46	41
3	-8	72	72
3	9	56	63
3	-9	82	89
3	11	47	49
3	-11	164	158
3	12	58	54
3	13	45	47
3	-13	51	62
6	9	76	59
6	-10	55	50
6	10	109	110
6	-11	72	78
6	11	40	21
6	-12	70	58
7	0	62	73
7	-1	82	90
7	-2	208	222
7	-3	51	35
7	4	36	19
7	-6	75	74
7	7	65	59
7	9	50	52
7	10	75	71
7	11	71	65
7	-12	69	77
8	-1	58	53
8	1	130	126
8	-3	73	60
8	-4	47	47
8	4	59	50
8	-5	77	78
8	5	78	68
8	6	65	51
8	-8	136	136
8	8	44	37
8	-9	63	56
8	9	53	45
8	-10	69	53
8	10	41	26
9	0	72	81
9	1	71	61
9	2	97	109
9	3	102	100
9	-3	40	19
9	4	75	71
9	-4	52	53
9	-7	59	76
10	0	41	47
10	-2	111	100
10	2	69	54
10	3	112	107
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1	1	98	110
1	-2	121	116
1	2	76	70
1	-3	112	112
1	4	48	43
1	-5	89	95
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1	6	129	136
1	-7	48	59
1	7	138	150
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1	8	174	169
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5	8	76	58
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5	9	97	92
5	-10	79	53
6	0	170	175
6	-1	93	86
6	-2	145	154
6	3	44	39
6	-3	86	87
6	4	102	100
6	-4	69	69
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6	5	47	20
6	6	84	69
6	-6	86	80
6	7	50	49
6	-7	93	99
6	8	41	39
6	-8	53	59
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6	-9	54	62
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7	1	51	42
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7	3	89	77
7	-4	56	40
7	4	72	74
7	-5	67	58
7	5	130	134
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7	7	77	66
7	-9	49	41
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8	3	82	88
8	-4	68	54
8	5	58	68
8	6	96	98
8	-7	57	45
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9	1	44	37
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9	3	91	25
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6	3	112	118
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6	7	154	153
6	8	118	113
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6	11	69	69
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6	15	70	54
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7	7	165	184
7	8	171	175
7	9	151	172
7	10	93	96
7	11	103	101
7	12	65	78
7	14	61	53
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8	3	42	39
8	4	107	107
8	5	227	229
8	6	110	106
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8	8	136	128
8	9	133	133
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8	11	89	70
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3	-3	59	44
3	3	196	195
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3	6	85	94
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3	7	144	136
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3	8	204	190
3	-9	119	104
3	-10	32	18
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3	15	155	143
3	16	48	52
3	17	86	80
3	18	40	19
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4	3	153	164
4	4	84	108
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4	5	75	81
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4	7	30	33
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4	8	108	117
4	-8	30	15
4	9	68	81
4	10	160	171
4	-10	89	90
4	11	90	90
4	-11	45	52
4	-12	86	94
4	13	44	42
4	14	132	135
4	-14	46	61
4	15	82	94
7	-8	42	29
7	8	131	111
7	-9	132	127
7	9	110	99
7	10	90	90
7	-11	134	130
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7	-12	48	38
7	14	70	49
7	-15	68	68
7	15	61	49
7	16	37	25
8	0	85	95
8	1	121	132
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8	-2	69	81
8	3	175	189
8	-3	174	196
8	4	135	137
8	-4	58	51
8	5	160	161
8	-5	99	110
8	6	53	48
8	-7	58	76
8	8	43	63
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8	9	66	63
8	10	87	98
8	-10	72	74
8	12	50	37
8	13	39	35
8	-13	102	115
8	14	39	54
8	-14	50	42
8	-15	93	96
9	0	75	71
9	-1	63	62
9	-2	70	74
9	-3	87	91
9	3	158	168
9	-4	156	159
9	4	128	121
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9	5	50	35
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9	6	37	27
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2	-9	30	45
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2	-12	74	78
2	13	112	92
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7	14	36	11
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8	5	38	18
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8	7	35	23
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8	11	41	18
8	-13	118	113
8	14	37	17
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9	1	55	60
9	-1	69	76
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9	4	45	25
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9	11	46	40
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2	-5	219	220
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2	12	48	62
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2	17	94	88
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3	3	148	141
3	4	125	111
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9	4	70	62
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9	11	91	74
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10	8	77	82
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11	-5	46	50
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4	6	182	177
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4	14	43	26
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5	1	119	112
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5	3	37	19
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5	5	77	85
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5	-6	147	155
5	7	47	42
5	8	122	124
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5	9	123	121
5	-9	128	119
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5	-12	57	61
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6	-1	110	99
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6	-3	135	119
6	3	97	93
6	-4	128	120
6	4	65	43
6	-5	108	100
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6	7	125	114
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2	-3	71	70
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2	8	39	11
2	-9	64	66
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6	-1	64	59
6	2	45	38
6	-3	38	5
6	3	49	48
6	4	77	64
6	4	48	48
7	0	51	48
7	1	50	61
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0	2	106	111
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1	-1	69	58
1	1	63	86
1	-2	72	78
1	2	73	79
2	1	56	66
2	-1	123	117
2	-2	40	10

TABLE 2

FINAL PARAMETERS IN NICKEL BIS(1,2-ETHENEDITHIOLATE)/2,3-DIMETHYLBUTADIENE

Atom	x^a	y	z	$B_{11}{}^b$	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.0412(4)	0.1445(2)	0.0610(2)	2.4(2)	3.8(2)	3.5(2)	0.2(1)	0.7(1)	0.6(1)
S_{11}	0.2141(8)	0.0178(5)	0.0705(3)	2.2(3)	4.1(4)	3.4(4)	0.5(3)	0.8(3)	0.7(3)
S_{12}	−0.0933(9)	0.1057(5)	0.1540(3)	2.9(4)	4.0(4)	3.3(4)	0.2(3)	0.5(3)	0.5(3)
S_{21}	−0.1201(9)	0.2772(5)	0.0472(3)	2.3(3)	3.7(4)	3.5(4)	−0.1(3)	1.1(3)	0.3(3)
S_{22}	0.1970(8)	0.1805(5)	−0.0260(3)	2.0(2)	4.1(4)	3.5(4)	0.2(3)	1.0(3)	0.3(3)
C_{11}	0.146(3)	−0.040(2)	0.143(1)	3.3(6)					
C_{12}	0.009(3)	−0.008(2)	0.179(1)	3.4(6)					
C_{13}	0.258(4)	−0.125(2)	0.166(1)	4.1(6)					
C_{14}	−0.065(4)	−0.054(2)	0.240(2)	4.3(7)					
F_{11}	0.357(2)	−0.160(1)	0.1153(8)	9 (1)	9 (1)	7 (1)	6 (1)	2.4(9)	3.5(9)
F_{12}	0.171(2)	−0.200(1)	0.1891(8)	6 (1)	3.2(8)	10 (1)	−1.2(7)	1.0(9)	1.2(8)
F_{13}	−0.383(2)	−0.097(1)	0.2120(7)	4.7(8)	6.2(9)	6.2(9)	0.6(7)	−2.0(9)	1.0(7)
F_{14}	−0.186(2)	0.007(1)	0.2688(7)	9 (1)	7 (1)	4.9(9)	0.1(8)	3.2(8)	1.9(8)
F_{15}	−0.159(2)	−0.134(1)	0.2296(7)	9 (1)	8 (1)	6 (1)	−4 (1)	3.1(8)	−1.2(9)
F_{16}	0.058(2)	−0.074(1)	0.2853(7)	8 (1)	7 (1)	2.9(7)	0.4(8)	0.1(8)	0.3(7)
C_{21}	−0.057(3)	0.325(2)	−0.030(1)	3.3(6)					
C_{22}	0.093(3)	0.285(2)	−0.059(1)	3.1(6)					
C_{23}	−0.160(3)	0.407(2)	−0.059(2)	4.3(7)					
C_{24}	0.192(3)	0.330(2)	−0.120(1)	3.2(6)					
F_{21}	−0.269(2)	0.448(1)	−0.0098(8)	5.7(9)	6 (1)	8 (1)	2.3(8)	2.0(8)	0.5(8)
F_{22}	−0.266(2)	0.387(1)	−0.1094(8)	4.4(8)	5.9(9)	7 (1)	1 (1)	−1.0(7)	−0.0(8)
F_{23}	−0.061(2)	0.485(1)	−0.0776(7)	5.9(9)	4 (1)	9 (1)	−0.4(7)	0.3(8)	1.5(8)
F_{24}	0.317(2)	0.272(1)	−0.1415(7)	5.6(9)	5.8(9)	8.8(9)	2.2(8)	3.2(7)	1.0(8)
F_{25}	0.090(2)	0.355(1)	−0.1663(7)	4.6(8)	6.2(9)	4.1(8)	0.6(7)	0.1(6)	0.3(7)
F_{26}	0.288(2)	0.408(1)	−0.0969(8)	6.0(9)	9 (1)	8 (1)	−4.1(9)	3.5(9)	−0.7(9)
C_1	−0.330(3)	0.076(2)	0.132(1)	3.3(6)					
C_2	−0.443(3)	0.169(2)	0.146(1)	2.5(5)					
C_3	−0.450(3)	0.242(2)	0.103(1)	3.1(5)					
C_4	−0.358(3)	0.233(2)	0.032(1)	4.0(6)					
C_5	−0.526(3)	0.169(2)	0.214(1)	3.8(6)					
C_6	−0.550(3)	0.339(2)	0.114(1)	4.2(6)					

[a] Estimated standard deviation of last significant figure given in parentheses [b] All temperature factors are in units of [Å]^2, with $B_{ij}=4b_{ij}/a_i^* a_j^*$ and $\mathrm{Tr}=\exp\left[-(h^2 b_{11}+k^2 b_{22}+l^2 b_{33}+2h\,k\,b_{12}+2h\,l\cdot b_{13}+2k\,l\,b_{23})\right]$

RESULTS AND DISCUSSION

Synthesis and properties

The straw-yellow adducts of nickel bis(1,2-ethenedithiolate) with 1,3-butadiene, 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene are readily prepared from (I) and the appropriate olefin in hydrocarbon solvents.

All three adducts decompose slowly in air with loss of olefin; butadiene being lost over a period of several hours while the 2,3-dimethyl-butadiene adduct, (III), is stable for several weeks. The materials are slightly soluble in hydrocarbon solvents, and very soluble in polar solvents (*e.g.* dichloromethane, 1,1,1-trichloroethane *etc.*) in which they disproportionate to give initially the monoanion of (I) and free olefin. Long periods of storage in the very polar solvents leads to complete decomposition with the predominant product being an insoluble violet powder which is tentatively

TABLE 3

BOND LENGTHS IN NICKEL BIS(1,2-ETHENEDITHIOLATE)/2,3-DIMETHYLBUTADIENE[a]

$Ni-S_{11}$	2 155(7)	$C_{13}-F_{11}$	1 35(3)
$Ni-S_{22}$	2 157(7)	$C_{13}-F_{12}$	1 29(3)
$Ni-S_{12}$	2 186(8)	$C_{13}-F_{13}$	1 34(3)
$Ni-S_{21}$	2 181(8)	$C_{14}-F_{14}$	1 36(3)
		$C_{14}-F_{15}$	1 30(3)
$S_{11}-C_{11}$	1 73(2)	$C_{14}-F_{16}$	1 31(3)
$S_{22}-C_{22}$	1 74(2)	$C_{23}-F_{21}$	1 39(3)
$S_{12}-C_{12}$	1 79(3)	$C_{23}-F_{22}$	1 31(3)
$S_{21}-C_{21}$	1 75(2)	$C_{23}-F_{23}$	1 35(3)
$S_{12}-C_{1}$	1 84(2)	$C_{24}-F_{24}$	1 30(3)
$S_{21}-C_{4}$	1 88(3)	$C_{24}-F_{25}$	1 24(3)
		$C_{24}-F_{26}$	1 35(3)
$C_{11}-C_{12}$	1 33(3)		
$C_{21}-C_{22}$	1 37(3)	⟨C-F⟩	1 33(4)
		$C_{2}-C_{3}$	1 30(3)
$C_{11}-C_{13}$	1 50(4)		
$C_{12}-C_{14}$	1 48(4)	$C_{1}-C_{2}$	1 55(3)
$C_{21}-C_{23}$	1 46(4)	$C_{3}-C_{4}$	1 59(3)
$C_{22}-C_{24}$	1.55(4)	$C_{2}-C_{5}$	1 51(3)
		$C_{3}-C_{6}$	1 54(3)
⟨C-C⟩	1 50(4)	⟨C-C⟩	1 54(3)

[a] Estimated Standard deviations of last significant figures in parentheses

TABLE 4

SELECTED BOND ANGLES IN NICKEL BIS(1,2-ETHENEDITHIOLATE)/2,3-DIMETHYLBUTADIENE

Angle (°)			
$S_{11}-Ni-S_{12}$	90 5(4)	$S_{11}-C_{11}-C_{13}$	123(2)
$S_{12}-Ni-S_{21}$	93 1(4)	$S_{11}-C_{11}-C_{12}$	117(2)
$S_{21}-Ni-S_{22}$	90.4(4)	$C_{12}-C_{11}-C_{13}$	121(2)
$S_{22}-Ni-S_{11}$	86'0(4)	$S_{12}-C_{12}-C_{14}$	116(2)
		$S_{12}-C_{12}-C_{11}$	117(2)
$Ni-S_{11}-C_{11}$	104 9(9)	$C_{11}-C_{12}-C_{14}$	127(2)
$Ni-S_{22}-C_{22}$	104 6(9)	$S_{21}-C_{21}-C_{23}$	119(2)
$Ni-S_{12}-C_{12}$	104 7(9)	$S_{21}-C_{21}-C_{22}$	117(2)
$Ni-S_{12}-C_{1}$	107.0(9)	$C_{22}-C_{21}-C_{23}$	124(2)
$C_{12}-S_{12}-C_{1}$	106 (1)	$S_{22}-C_{22}-C_{24}$	114(2)
$Ni-S_{21}-C_{21}$	105 5(9)	$S_{22}-C_{22}-C_{21}$	122(2)
$Ni-S_{21}-C_{4}$	105 1(9)	$C_{21}-C_{22}-C_{24}$	124(2)
$C_{21}-S_{21}-C_{4}$	104 (1)		
$S_{12}-C_{1}-C_{2}$	107 (1)	⟨C-C-F⟩	113(3)
$C_{1}-C_{2}-C_{3}$	122 (2)		
$C_{1}-C_{2}-C_{5}$	113 (2)		
$C_{3}-C_{2}-C_{5}$	126 (2)	⟨F-C-F⟩	106(3)
$C_{2}-C_{3}-C_{4}$	121 (2)		
$C_{2}-C_{3}-C_{6}$	125 (2)		
$C_{4}-C_{3}-C_{6}$	114 (2)		
$S_{21}-C_{4}-C_{3}$	104 (2)		

TABLE 5

SOME BEST LEAST-SQUARE PLANES IN NICKEL BIS(1,2-ETHENEDITHIOLATE)/2,3-DIMETHYLBUTADIENE

Atom	*Used in fitting plane*	*Distance from plane (Å)*
	Plane 1	
Ni	[a]	0.040(3)
S_{11}	[a]	0.015(6)
S_{12}	[a]	−0.033(7)
S_{21}	[a]	0.013(7)
S_{22}	[a]	−0.034(6)
C_1		1.56
C_2		1.28
C_3		1.25
C_4		1.64
C_5		0.95
C_6		0.92
	$0.651x+0.527y+0.546z=1.93$	
	Plane 2	
C_1	[a]	−0.035(23)
C_2	[a]	0.029(21)
C_3	[a]	−0.009(22)
C_4	[a]	0.024(24)
C_5	[a]	0.015(23)
C_6	[a]	−0.025(19)
S_{11}		−2.55
S_{12}		−1.81
S_{21}		−1.79
S_{22}		−2.62
	$0.823x+0.410y+0.393z=-0.612$	
The angle between plane 1 and 2 is 14.9°		

[a] Means this atom contributed to the least square fit of the plane

formulated as a polymeric metal–sulfur bridged complex on the basis of its infrared spectrum and its reaction with Lewis bases to give the monoanion of (I).

Cycloaddition products analogous to (III) have been formed with a variety of other conjugated olefins (1,3-pentadiene, cyclopentadiene, *cis*, *trans*- and *trans*, *trans*-2,4-hexadiene, and 1,3-cyclohexadiene), but none of these have been isolated and they have been characterized only by their optical spectra.

Consistent with the previous description of this reaction as an oxidative cycloaddition 1,3-hexachlorobutadiene fails to show any reaction with (I).

Structure of the nickel bis(1,2-ethenedithiolate)/2,3-dimethylbutadiene adduct★

Cycloaddition product (III), is as shown in Fig. 2, an undistorted square planar monomer in which the addition of the olefin has produced a third chelate ring. Ligation occurs via formation of an identical pair of sulfur–carbon bonds between *cis*-sulfur atoms and the 1,4-carbon atoms of the diolefin. The newly formed carbon–sulfur bonds, approximately 0.1 Å longer than the corresponding bonds

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★ See Note added in Proof.

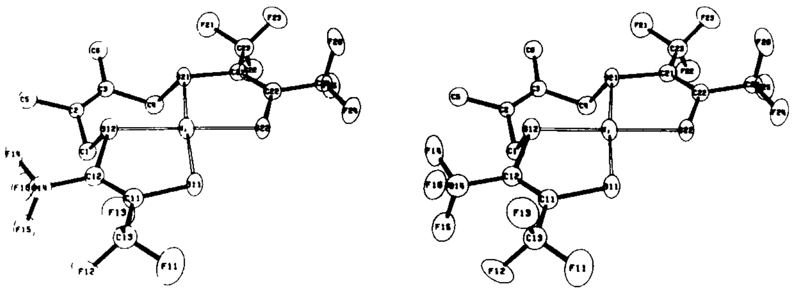

Fig 2. The adduct In this particular case, the Nickel bis[1,2-bis(trifluoromethyl)1,2-ethenedithiolate/2,3-dimethylbutadiene adduct is shown this is a stereopair and can best be seen with the aid of a hand viewer

in the nickel bis(1,2-ethenedithiolate) moiety, are very reasonable lengths for C–S single bonds[6]. Planarity of the NiS_4 unit in (III) as contrasted with the extreme warping of the plane in nickel bis(1,2-ethenedithiolate)/norbornadiene[1] is a consequence of the strain-free seven-membered chelate ring in the former.

The bound olefin, also planar, deviates from being parallel to the NiS_4 plane by 15°. Tetrahedral hybridization for C_1 and C_4 is clearly indicated by the bond angles and lengths around these carbons as well as the observed ^1H geminal coupling constant of 13.5 Hz[3,7]. Shrinkage of the C_2–C_3 bond to 1.30 Å is a further indication of the major role played by the π electronic structure of the olefin in the cycloaddition reaction.

Besides conversion of two sulfur atoms to the tetrahedral stereochemistry required by the new adduct S–C bonds, the significant structural features of the nickel bis(1,2-ethenedithiolate) moiety are the increase in nickel–sulfur and sulfur–carbon and decrease in ethene carbon–carbon bond lengths over the corresponding parameters in (I)[8]. Both ESR studies[9] and HMO calculations[10] indicate that the lowest unoccupied MO of (I) is Ni–S, S–C antibonding and C–C bonding (Fig. 1a); thus the bond length changes resulting from adduct formation imply that (I) has served the role of an acceptor or π acid. As pointed out in previous reports of this series[1,3] the IR and UV-visible spectra as well as the electrochemistry corroborate that (I) accepts π electron density from olefins in the cycloaddition reactions.

CONCLUSION

Dienes and olefins form cycloaddition products with nickel bis(1,2-ethenedithiolate) which are close structural relatives. This fact along with the evidence that the reactions are redox in nature, (an alternate, but equivalent description would be π acid-base reaction), further corroborates the orbital correlation scheme presented earlier in an attempt to unify the description of these reactions.

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NOTE ADDED IN PROOF

Clark *et al.*[11] have recently given the structure of Palladium bis(*cis*-1,2-diphenylethylene-1,2-dithiolate)/Cyclohexa-1,3-diene adduct. Their conclusions are consistent with this report in every respect

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