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The Crystal and Molecular Structure of a Nickel(II) Iodide Complex of a Macrocyclic Tetradentate Imine Ether

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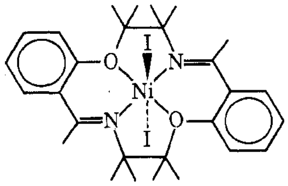
The crystal structure of Ni($C_{18}H_{18}N_2O_2$)I_2 where $C_{18}H_{18}N_2O_2$ is the tetradentate macrocyclic ligand 1,8-diaza-3,4,10,11-dibenzo-5,12-dioxo-1,3,8,10-cyclotetradecatetraene was determined by single-crystal X-ray diffraction using automatic diffractometer methods to collect three-dimensional data. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares methods to a conventional residual $R_1 = 0.047$ and a weighted residual $R_2 = 0.058$ based on 943 reflections with $I_{\text{obsd}} > 3\sigma(I)$. The compound crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a = 7.607$ (5) Å, $b = 15.582$ (11) Å, $c = 8.215$ (5) Å, and $\beta = 98.17$ (2)°. The density calculated for $Z = 2$ is 2.09 (1) g/cm^3 as compared with a measured density of 2.07 (4) g/cm^3. The structure consists of discrete molecules with the nickel atom at a center of inversion. The two nitrogen and two oxygen atoms of the macrocyclic ligand define a plane, with respect to which the iodine atoms occupy apical positions at a distance of 2.880 (3) Å from the nickel atom. The in-plane Ni–N and Ni–O distances are 1.92 (1) and 2.07 (1) Å, respectively. The benzo groups are inclined at an angle of 14.6° with respect to the coordination plane.

Introduction

Kluiber and Sasso[1] have recently reported that bis(*N*-2-bromoethylsalicylaldiminato)nickel(II) reacts with sodium iodide in acetone to form a paramagnetic ($\mu_{\text{eff}} = 3.12$ BM) complex of empirical formula Ni($C_{18}H_8N_2O_2$)I_2. Although they strongly suspected that the product was a complex of a roughly planar tetradentate macrocyclic imine ether ligand with the iodine atoms coordinated above and below the plane (see structure I), they could not absolutely exclude alternative formulations on the basis of their evidence. The present structure determination was undertaken to characterize definitively the product of this interesting new example of a template reaction and to determine the geometrical details of the new macrocyclic ligand 1,8-diaza-3,4,10,11-dibenzo-5,12-dioxo-1,3,8,10-cyclotetradecatetraene.



I

There is considerable current interest in the synthesis, properties, and structures of complexes of macrocyclic ligands. Particularly pertinent to the present investigation are the recently reported[2] structures of the high-spin tetragonal Ni(TAAB)$I_2 \cdot H_2O$ and low-spin planar Ni(TAAB)$(BF_4)_3$ complexes (TAAB[3] is a tetradentate macrocyclic ligand with four equivalent nitrogen donor atoms). Structures of several other macrocyclic Schiff base complexes involving only nitrogen donor atoms have appeared.[4]

While imine thioether macrocycles formed in template reactions[5] are well known, the present ligand is apparently the first example of a macrocycle containing an ether linkage formed in such a manner. Indeed, transition metal–ether complexes of any sort are quite rare and structural characterization of bonds of this sort is desirable. Furthermore current interest is high in ether complexes,[6] particularly complexes of alkali metals which may be of importance in biological transfer processes.

Experimental Section

Preliminary Crystal Data.—Orange crystals of $C_{18}H_{18}I_2N_2NiO_2$ were kindly supplied by Professor R. W. Kluiber of Rutgers, The State University, Newark, N. J. Preliminary Weissenberg photographs of the 0*kl*, 1*kl*, and *h*0*l* layers with Cu Kα radiation showed systematic extinctions: 0*k*0, $k = 2n + 1$, and *h*0*l*, $l = 2n + 1$ uniquely determining the space group $P2_1/c$ (C_{2h}^5, no. 14). A crystal of irregular shape (roughly resembling a capped paraboloid) of approximate dimensions 0.12 × 0.10 × 0.08 mm was chosen for accurate cell dimension and intensity measurements. It was mounted on a glass fiber with the a^* axis of the monoclinic cell parallel to the spindle axis (φ) of the four-circle Syntex computer controlled X-ray diffractometer equipped with a scintillation counter and pulse height analyzer. Unit cell dimensions were determined from a least-squares analysis[7] of 13 accurately centered, high 2θ reflections. These and the final intensity data were obtained at room temperature (17°) using nickel-filtered (at the X-ray source) copper radiation (Cu Kα_1, λ 1.54051 Å). The results are $a = 7.607$ (5) Å, $b = 15.582$ (11) Å, $c = 8.215$ (5) Å, $\beta = 98.17$ (2)°, and $V = 963.8$ (5) Å^3. Standard deviations of the least significant figure(s) here and in the tables are given in parentheses. The density calculated for two molecules per unit cell is 2.091 g/cm^3. The density found by flotation in a

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[1] R. W. Kluiber and G. Sasso, *Inorg. Chim. Acta*, **4**, 226 (1970).

[2] S. W. Hawkinson and E. B. Fleischer, *Inorg. Chem.*, **8**, 2402 (1969).

[3] Tetrabenzo[*b,f,j,n*][1,5,9,13]tetraazacyclohexadecine.

[4] (a) I. E. Maxwell and M. F. Bailey, *Chem. Commun.*, 883 (1966); (b) M. F. Bailey and I. E. Maxwell, *ibid.*, 908 (1966); (c) R. R. Ryan, B. T. Kilbourn, and J. D. Dunitz, *ibid.*, 910 (1966); (d) E. B. Fleischer and E. Klein, *Inorg. Chem.*, **4**, 637 (1965).

[5] M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 3651 (1964).

[6] See, for instance, D. Bright and M. R. Truter, *Nature* (*London*), **225**, 176 (1970); C. J. Peterson, *J. Amer. Chem. Soc.*, **92**, 386 (1970).

[7] Computations were performed on an IBM 360-67 at the Computation Center of The Pennsylvania State University. The following programs were used for the operations indicated: refinement of cell dimensions, Hope's CELDIM; conversion of paper-tape diffractometer output to IBM cards, Stanko's PTAPE; absorption and *Lp* corrections, Prewitt's ACAC; Patterson function and Fourier synthesis, Zalkin's FORDAP; least-squares refinement, the Brown University version of Busing and Levy's ORFLS; interatomic distance and angle computation, Zalkin's DISTAN; calculation of least-squares planes, Chu's LSPLAN; preparation of Table I, Zalkin's LIST; position of hydrogen atoms, Zalkin's HFINDR; stereoviews, Johnson's ORTEP.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $Ni(C_{18}H_{18}N_2O_2)I_2$[a]

L	FOB	FCA
H,K=	0,	0
-8	18	17
-6	7	7*
-4	60	66
-2	37	36
2	37	36
4	62	66
6	12	7
8	19	17
H,K=	0,	1
-8	12	11
-7	58	59
-6	32	34
-5	83	87
-4	44	46
-3	96	101
-2	31	33
-1	65	66
1	63	66
2	31	33
3	98	101
4	46	46
5	87	87
6	35	34
7	62	59
8	15	11
H,K=	0,	2
-8	9	8*
-7	8	14*
-6	17	17
-5	14	15
-4	48	49
-3	69	75
-2	121	123
-1	104	97
0	144	139
1	96	97
2	119	123
3	71	75
4	50	49
5	18	15
6	17	17
7	17	14
8	8	8*
H,K=	0,	3
-8	38	39
-7	35	35
-6	64	65
-5	15	14
-4	96	101
-3	73	74
-2	90	88
-1	16	15
1	14	15
2	88	88
3	74	74
4	100	101
5	14	14
6	68	65
7	35	35
H,K=	0,	4
-8	7	8*
-7	18	17
-6	16	14
-5	20	19
-4	24	25
-3	70	75
-2	27	25
-1	167	161
0	30	26
1	160	161
2	26	25
3	71	75
4	24	25
5	22	19
6	17	14
7	19	17
H,K=	0,	5
-8	27	26
-7	9	3*
-6	75	77
-5	43	46
-4	84	85
-3	9	6*
-2	48	49
-1	40	39
1	38	39
2	46	49
3	10	6
4	85	89
5	47	46
6	81	77
7	13	3
H,K=	0,	6
-7	0	4*
-6	15	13
-5	12	8
-4	5	7*
-3	35	36
-2	134	133
-1	121	116
0	40	40
1	117	116
2	131	133
3	35	36
4	11	7*
5	7	8*
6	15	13
7	0	4*
H,K=	0,	7
-7	32	32
-6	23	23
-5	65	67
-4	42	44
-3	39	39
-2	13	9
-1	82	79
1	79	79
2	10	9
3	39	39
4	45	44
5	69	67
6	23	23
7	34	32
H,K=	0,	8
-7	7	3*
-6	6	0*
-5	12	4
-4	31	34
-3	11	9
-2	111	111
-1	11	8
0	100	99
1	13	8
2	109	111
3	12	9
4	34	34
5	7	4*
6	3	0*
H,K=	0,	9
-7	25	25
-6	21	22
-5	57	62
-4	23	23
-3	40	40
-2	12	7
-1	50	46
1	47	46
2	12	7
3	42	40
4	25	23
5	63	62
6	23	22
H,K=	0,	10
-6	9	8*
-5	8	2*
-4	15	10
-3	29	31
-2	73	73
-1	50	50
0	43	43
1	49	50
2	73	73
3	33	31
4	13	10
5	12	2*
6	12	8
H,K=	0,	11
-6	30	32
-5	31	34
-4	47	48
-3	13	7
-2	29	30
-1	31	28
1	28	28
2	29	30
3	13	7
4	49	48
5	33	34
H,K=	0,	12
-5	14	15
-4	10	13*
-3	25	27
-2	23	21
-1	64	63
0	20	17
1	63	63
2	22	21
3	26	27
4	11	13*
5	16	15
H,K=	0,	13
-5	3	4*
-4	30	32
-3	15	15
-2	26	27
-1	12	13*
1	13	13
2	28	27
3	15	15
4	32	32
H,K=	0,	14
-4	12	13
-3	28	30
-2	17	15
-1	32	31
0	49	48
1	34	31
2	18	15
3	30	30
H,K=	0,	15
-3	25	29
-2	13	12
-1	14	9
1	15	9
2	13	12
H,K=	1,	0
-8	50	47
-6	56	57
-4	134	145
-2	132	134
0	132	131
2	185	189
4	54	58
6	81	80
H,K=	1,	1
-8	14	13
-7	45	42
-6	15	13
-5	19	18
-4	29	30
-3	56	61
-2	47	48
-1	164	165
0	10	10
1	56	56
2	177	180
3	151	155
4	11	8
5	30	30
6	12	4
7	4	2*
H,K=	1,	2
-8	32	31
-7	34	34
-6	43	45
-5	56	57
-4	95	100
-3	99	103
-2	67	69
-1	33	30
0	73	68
1	37	36
2	81	80
3	29	31
4	54	55
5	47	47
6	61	59
7	47	45
H,K=	1,	3
-8	34	33
-7	26	25
-6	14	16
-5	25	24
-4	32	32
-3	9	5*
-2	114	111
-1	80	77
0	189	186
1	44	44
2	131	135
3	75	76
4	80	79
5	6	6*
6	12	3
7	8	6*
H,K=	1,	4
-8	15	12
-7	44	43
-6	25	26
-5	77	80
-4	40	40
-3	107	110
-2	31	29
-1	96	93
0	15	15
1	25	26
2	32	34
3	69	71
4	29	29
5	72	71
6	14	13
7	50	48
H,K=	1,	5
-8	31	29
-7	8	10*
-6	21	20
-5	26	29
-4	40	43
-3	46	48
-2	102	100
-1	14	13
0	150	148
1	76	75
2	101	103
3	8	5*
4	81	80
5	32	31
6	14	8
7	12	9*
H,K=	1,	6
-7	28	29
-6	54	57
-5	58	59
-4	53	57
-3	61	61
-2	80	79
-1	59	56
0	22	19
1	7	1*
2	14	14
3	66	66
4	73	74
5	42	43
6	27	27
H,K=	1,	7
-7	14	14
-6	3	5*
-5	10	5*
-4	6	2*
-3	54	53
-2	60	58
-1	49	45
0	30	31
1	148	149
2	54	54
3	48	49
4	21	21
5	32	32
6	13	8
H,K=	1,	8
-7	12	10
-6	57	59
-5	0	4*
-4	65	70
-3	7	4*
-2	103	100
-1	7	6*
0	22	21
1	8	5*
2	14	12
3	7	1*
4	65	65
5	13	7
6	49	47
H,K=	1,	9
-7	13	10
-6	0	4*
-5	10	9*
-4	11	6*
-3	50	52
-2	30	28
-1	59	58
0	27	27
1	109	109
2	36	33
3	44	45
4	16	15
5	30	31
6	0	7*
H,K=	1,	10
-6	41	45
-5	29	30
-4	27	27
-3	36	36
-2	61	60
-1	28	25
0	12	8
1	6	1*
2	6	4*
3	24	25
4	47	48
5	29	28
H,K=	1,	11
-6	12	9
-5	20	18
-4	11	9*
-3	39	40
-2	57	52
-1	10	9*
0	63	65
1	56	56
2	60	59
3	7	8*
4	33	32
5	12	14*
H,K=	1,	12
-5	37	37
-4	14	8
-3	41	45
-2	9	10*
-1	30	29
0	13	15
1	9	6*
2	19	16
3	29	28
4	15	17
H,K=	1,	13
-5	8	5*
-4	17	18
-3	13	7
-2	28	28
-1	15	9
0	54	54
1	9	2*
2	47	46
3	28	26
4	27	25
H,K=	1,	14
-4	26	30
-3	28	28
-2	17	15
-1	17	15
0	18	17
1	10	5*
2	21	23
3	15	13
H,K=	1,	15
-3	9	3*
-1	37	41
0	17	18
1	15	16
H,K=	2,	0
-8	48	46
-6	15	17
-4	34	35
-2	148	148
0	177	172
2	146	146
4	93	94
6	18	21
H,K=	2,	1
-8	6	9*
-7	28	26
-6	31	30
-5	105	110
-4	38	41
-3	72	76
-2	46	48
-1	118	114
0	47	47
1	10	7*
2	26	26
3	12	9
4	63	64
5	78	77
6	15	13
7	41	39
H,K=	2,	2
-8	35	34
-7	27	25
-6	14	9
-5	10	8*
-4	13	14
-3	14	13
-2	85	81
-1	106	99
0	107	101
1	109	107
2	166	162
3	40	41
4	9	11*
5	43	44
6	38	38
7	10	9*
H,K=	2,	3
-8	21	18
-7	14	7
-6	61	62
-5	56	58
-4	117	122
-3	18	18
-2	89	90
-1	60	58
0	71	71
1	0	2*
3	16	13
4	63	62
5	50	50
6	66	65
7	14	13
H,K=	2,	4
-8	12	8
-7	31	30
-6	24	22
-5	17	17
-4	37	36
-3	21	21
-2	49	46
-1	120	118
0	27	27
1	135	135
2	26	29
3	97	100
4	28	27
5	38	37
6	18	14
7	10	9*
H,K=	2,	5
-8	24	22
-7	26	27
-6	63	63
-5	9	5*
-4	84	89
-3	56	55
-2	110	106
-1	14	14
0	48	49
1	36	34
2	21	21
3	42	42
4	43	44
5	0	5*
6	57	57
7	24	22
H,K=	2,	6
-7	22	21
-6	39	41
-5	20	20
-4	23	23
-3	41	41
-2	49	53
-1	61	57
0	89	89
1	82	83
2	59	59
3	70	72
4	58	58
5	28	26
6	13	10*
H,K=	2,	7
-7	40	39
-6	23	23
-5	34	34
-4	30	31
-3	94	93
-2	41	39
-1	43	45
0	21	17
1	48	49
2	10	8
3	51	50
4	24	25
5	39	38
6	18	15
H,K=	2,	8
-7	10	6*
-6	35	33
-5	7	7*
-4	23	22
-3	6	1*
-2	36	38
-1	11	9
0	134	135
1	17	17
2	55	55
3	8	1*
4	74	71
5	0	3*
6	11	10*
H,K=	2,	9
-7	25	28
-6	20	20
-5	43	44
-4	18	15
-3	82	81
-2	30	32
-1	29	30
0	20	19
1	36	37
2	0	5*
3	43	42
4	14	13
5	30	30
H,K=	2,	10
-6	21	21
-5	13	11
-4	22	22
-3	23	19
-2	11	11*
-1	27	27
0	79	77
1	47	48
2	37	37
3	32	33
4	42	42
5	19	20
H,K=	2,	11
-6	23	27
-5	4	6*
-4	46	49
-3	44	45
-2	50	48
-1	5	3*
0	33	30
1	22	20
2	12	5
3	29	28
4	30	30
H,K=	2,	12
-5	5	6*
-4	16	15
-3	10	9*
-2	12	1*
-1	57	57
0	9	6*
1	42	44
2	10	7*
3	43	43
4	15	13
H,K=	2,	13
-5	21	18
-4	36	36
-3	7	3*
-2	35	34
-1	12	12*
0	21	23
1	10	0*
2	5	6*
3	10	9*
H,K=	2,	14
-4	12	13
-3	15	14
-2	25	28
-1	21	20
0	21	16
1	43	40
2	34	35
H,K=	3,	0
-8	12	9
-6	66	68
-4	78	81
-2	170	174
0	56	59
2	23	24
4	37	35
6	58	59
H,K=	3,	1
-8	14	12
-7	31	32
-6	17	16
-5	52	51
-4	10	4
-3	57	59
-2	0	4*
-1	29	29
0	64	63
1	137	133
2	52	53
3	82	85
4	24	24
5	56	55
6	20	19
H,K=	3,	2
-8	9	7*
-7	26	24
-6	51	51
-5	49	49
-4	43	45
-3	71	77
-2	137	138
-1	76	69
0	28	28
1	27	26
2	19	18
3	19	19
4	55	53
5	22	22
6	10	12*
H,K=	3,	3
-8	37	33
-7	8	7*
-6	38	42
-5	30	28
-4	15	16
-3	32	32
-2	73	70
-1	11	6
0	83	79
1	65	65
2	118	117
3	20	20
4	83	82
5	45	46
6	23	22
H,K=	3,	4
-8	11	11*
-7	23	23
-6	22	21
-5	65	67
-4	21	20
-3	96	97
-2	19	18
-1	105	102
0	15	14
1	32	33
2	14	15
3	12	14
4	26	26
5	40	41
6	17	14
H,K=	3,	5
-7	25	25
-5	14	15
-4	11	5
-3	24	25
-2	38	38
-1	26	22
0	109	108
1	27	28
2	92	93
3	46	49
4	67	66
5	6	3*
6	26	24
H,K=	3,	6
-7	21	19
-6	19	18
-5	40	40
-4	85	90
-3	70	71
-2	43	43
-1	57	57
0	59	54
1	23	23
2	7	6*
3	9	10*
4	7	8*
5	29	28
6	29	30
H,K=	3,	7
-7	33	33
-6	18	15
-5	4	4*
-4	10	7*
-3	32	31
-2	17	16
-1	80	74
0	29	27
1	60	59
2	48	49
3	79	80
4	17	19
5	30	27
H,K=	3,	8
-7	7	6*
-6	29	29
-5	0	3*
-4	90	93
-3	12	11*
-2	52	52
-1	5	8*
0	76	73
1	8	4*
2	10	12*
3	12	7*
4	11	12*
5	11	3*
H,K=	3,	9
-6	13	11
-5	16	12
-4	10	1*
-3	9	6*
-2	5	2*
-1	71	66
0	26	27
1	45	45
2	27	29
3	70	75
4	15	12
5	15	18
H,K=	3,	10
-6	18	16
-5	18	19
-4	46	48
-3	44	46
-2	33	32
-1	30	26
0	47	43
1	18	17
2	14	13
3	10	3*
4	10	6*
H,K=	3,	11
-5	13	6
-4	10	4*
-3	7	8*
-2	21	19
-1	29	30
0	35	35
1	23	24
2	59	59
3	24	27
4	34	34
H,K=	3,	12
-5	32	31
-4	17	17
-3	43	44
-2	14	15
-1	42	43
0	7	8*
1	8	7*
2	9	8*
3	5	2*
H,K=	3,	13
-4	4	4*
-3	14	13
-2	13	14*
-1	12	14*
0	38	39
1	22	23
2	36	36
H,K=	3,	14
-3	23	26
-2	14	36
-1	21	20
0	10	5*
H,K=	4,	0
-6	54	52
-4	11	10*
-2	11	14*
0	111	105
2	89	90
4	78	80
6	28	28
H,K=	4,	1
-7	21	19
-6	13	12*
-5	42	44
-4	28	29
-3	110	114
-2	44	44
-1	47	48
0	40	40
1	81	79
2	9	9*
3	14	10
4	13	10
5	19	22
6	6	4*
H,K=	4,	2
-7	34	32
-6	45	43
-5	30	30
-4	12	7
-3	12	9
-2	18	16
-1	47	46
0	108	105
1	51	49
2	40	39
3	55	54
4	57	59
5	38	39
6	21	19
H,K=	4,	3
-7	23	26
-6	41	41
-5	0	5*
-4	68	68
-3	57	57
-2	95	94
-1	15	12
0	87	86
1	44	42
2	26	27
3	17	13
4	21	21
5	5	2*
6	30	30
H,K=	4,	4
-7	35	34
-6	19	19
-5	40	42
-4	29	25
-3	6	2*
-2	17	17
-1	43	39
0	14	11
1	76	75
2	11	4
3	73	74
4	5	8*
5	45	45
H,K=	4,	5
-7	4	2*
-6	30	30
-5	27	27
-4	74	74
-3	7	5*
-2	92	92
-1	52	50
0	63	62
1	14	11
2	22	21
3	11	10*
4	16	14
5	15	17
H,K=	4,	6
-7	28	26
-6	29	25
-5	15	17
-4	34	34
-3	9	8*
-2	43	41
-1	25	25
0	18	18
1	64	62
2	65	66
3	44	45
4	28	26
5	29	28
H,K=	4,	7
-7	9	7*
-6	13	14
-5	42	44
-4	32	31
-3	32	33
-2	29	26
-1	96	93
0	20	19
1	22	21
2	10	14*
3	15	12
4	15	13
5	24	25
H,K=	4,	8
-6	28	29
-5	0	1*
-4	37	35
-3	9	6*
-2	49	47
-1	19	16
0	26	26
1	6	11*
2	73	73
3	9	1*
4	43	43
H,K=	4,	9
-6	8	6*
-5	41	43
-4	19	15
-3	34	36
-2	30	28
-1	77	77
0	20	20
1	19	16
2	12	7
3	14	9
4	0	3*
H,K=	4,	10
-5	15	13
-4	18	20
-3	14	13
-2	22	23
-1	16	19
0	24	24
1	28	26
2	41	41
3	23	21
H,K=	4,	11
-5	21	23
-4	36	35
-3	16	14
-2	36	37
-1	29	30
0	40	41
1	5	4*
2	19	17
3	9	1*
H,K=	4,	12
-4	5	6*
-3	9	2*
-2	16	15
-1	22	22
0	8	10*
1	30	30
2	17	16
H,K=	4,	13
-3	17	19
-2	16	34
-1	8	4*
0	28	28
H,K=	5,	0
-6	23	25
-4	70	69
-2	63	67
0	109	108
2	23	25
4	6	3*
H,K=	5,	1
-7	38	40
-6	20	19
-5	34	34
-4	11	11*
-3	35	34
-2	0	1*
-1	44	43
0	16	13
1	34	35
2	21	22
3	65	69
4	27	28
5	21	33
H,K=	5,	2
-7	6	4*
-6	5	3*
-5	19	16
-4	63	63
-3	57	58
-2	44	45
-1	60	59
0	79	76
1	29	28
2	11	7*
3	16	16
4	14	9
5	3	6*
H,K=	5,	3
-6	41	41
-5	15	8
-4	27	23
-3	31	26
-2	6	10*
-1	36	32
0	35	33
1	8	4*
2	75	75
3	36	39
4	42	43
5	14	12
H,K=	5,	4
-7	6	3*
-6	14	12
-5	42	40
-4	9	13*
-3	61	63
-2	10	11*
-1	72	69
0	23	22
1	51	51
2	21	17
3	18	19
4	11	2*
H,K=	5,	5
-6	32	33
-5	19	20
-4	39	40
-3	7	2*
-2	9	6*
-1	16	15
0	47	45
1	34	33
2	48	48
3	9	8*
4	46	51
H,K=	5,	6
-6	20	19
-5	28	26
-4	30	26
-3	38	39
-2	68	67
-1	47	47
0	25	25
1	42	39
2	36	35
3	13	2
4	11	8*
H,K=	5,	7
-6	8	13*
-5	31	33
-4	10	9*
-3	0	5*
-2	10	5*
-1	9	9*
0	20	19
1	50	50
2	19	18
3	36	35
4	19	20
H,K=	5,	8
-5	0	3*
-4	35	35
-3	11	6*
-2	76	75
-1	8	11*
0	33	31
1	9	3*
2	35	36
3	9	5*
H,K=	5,	9
-5	31	34
-4	17	15
-3	11	3*
-2	10	7*
-1	13	11
0	21	15
1	52	54
2	8	8*
3	30	32
H,K=	5,	10
-3	25	23
-2	46	47
-1	27	26
0	19	12
1	23	22
2	20	22
H,K=	5,	11
-4	18	13
-2	3	3*
-1	5	3*
0	13	13*
1	23	23
H,K=	5,	12
-2	11	9
H,K=	6,	0
-6	30	31
-4	45	47
-2	11	3*
0	16	10
2	51	54
H,K=	6,	1
-6	11	4
-5	28	31
-3	33	33
-2	19	16
-1	70	76
0	22	24
1	33	34
2	17	18
3	23	25
H,K=	6,	2
-6	17	17
-5	20	21
-4	36	41
-3	33	33
-2	3	10*
-1	8	9*
0	8	4*
1	23	22
2	43	44
3	25	28
H,K=	6,	3
-6	14	11
-5	24	22
-4	36	35
-3	14	12
-2	60	58
-1	35	34
0	56	58
1	12	4
2	34	34
3	24	21
H,K=	6,	4
-6	14	14
-5	39	39
-4	7	10*
-3	14	15*
-2	11	3*
-1	12	4*
0	11	3*
1	31	30
2	21	20
3	38	38
H,K=	6,	5
-5	11	11*
-4	29	30
-3	20	22
-2	61	59
-1	18	11
0	53	53
1	27	29
2	24	27
3	12	6*
H,K=	6,	6
-5	23	23
-4	14	14
-3	17	13
-2	23	20
-1	11	5*
0	24	23
1	18	19
2	13	12
H,K=	6,	7
-5	10	5*
-4	15	16
-3	42	40
-2	19	20
-1	32	31
0	21	19
1	42	44
2	11	8*
H,K=	6,	8
-4	17	15
-3	15	4
-2	22	20
-1	10	7*
0	24	26
1	8	5*
H,K=	6,	9
-4	5	5*
-3	36	38
-2	19	16
-1	28	28
0	21	16
H,K=	6,	10
-3	14	13
-2	9	6*
H,K=	7,	0
-4	19	14
-2	53	63
0	34	34
H,K=	7,	1
-5	41	39
-4	13	13*
-3	13	14*
-2	5	2*
-1	18	22
0	4	5*
1	27	27
H,K=	7,	2
-5	13	4
-4	0	8*
-3	22	19
-2	33	38
-1	31	33
0	27	28
1	28	27
H,K=	7,	3
-4	32	32
-3	9	3*
-2	20	20
-1	12	1*
0	14	11
1	12	10*
H,K=	7,	4
-4	9	12*
-3	30	28
-2	13	10
-1	33	38
0	3	2*
1	36	40
H,K=	7,	5
-4	27	27
-3	21	23
-2	18	18
-1	10	5*
0	8	5*
H,K=	7,	6
-3	23	23
-2	8	15*
H,K=	7,	7
-2	0	1*

[a] The asterisks indicate data not used in the refinement.

mixture of carbon tetrachloride and methyl iodide was 2.07 (4) g/cm³.

Collection and Reduction of Intensity Data.—Intensity data were collected by the θ–2θ scan technique with the scan covering a range of 1.5° on each side of the calculated peak position at a rate of 1.0°/min. A 15-sec stationary background count was taken at each end of the scan range. The net intensity I and its standard deviation $\sigma(I)$ were calculated from the relations $I = S - \alpha(B_1 + B_2)$ and $\sigma(I)^2 = S + \alpha^2(B_1 + B_2) + (dS)^2$ where S is the total accumulated scan count, α is the ratio of the scan time to the total background time, B_1 and B_2 are the background counts, and d is an empirical constant to account for nonrandom errors here taken as 0.04. Three check reflections were measured every 104 reflections throughout the data collection and showed random variations of $\pm 5\%$ for $I = 4000$ and $\pm 3\%$ for $I = 12{,}000$. A total of 1155 reflections (not including space group extinctions which were all below $3\sigma(I)$ and were deleted from the data set) were measured to a limiting $(\sin\theta)/\lambda$ of 0.519; of these 943 had $I \geq 3\sigma(I)$ and were used in the refinement. Observed structure factors on an arbitrary scale were obtained by applying Lorentz (L), polarization (p), and absorption corrections (A) to the measured intensities:[7] $|F_o| = [I/ALp]^{1/2}$. The standard deviations of observed structure factors $\sigma(F)$ were computed by $\sigma(F) = \sigma(I)/2ALp|F_o|$. The 400 reflection showed variations in $I^{1/2}$ of from 100 to 74 on a relative scale during a 360° rotation about the φ axis at $\chi = 90°$. Application of an absorption correction[7] with $\mu = 271.7$ cm^{-1} reduced this variation to between 100 and 91 using 256 integration points. Transmission factors A varied between 0.14 and 0.30 for the entire data set.

Solutions and Refinement of the Structure.—With two molecules per unit cell the nickel atom was required to lie at a special position (the 0, 0, 0 and 0, $^1/_2$, $^1/_2$ set of inversion centers was chosen). A three-dimensional Patterson synthesis[7] located the position of the iodine atom and two cycles of least-squares refinement[7] with these two atoms yielded residuals[8] $R_1 = 0.211$ and $R_2 = 0.265$. The function minimized in all least-squares refinements was $\Sigma w(|F_o| - |F_c|)^2$. A three-dimensional Fourier synthesis, phased on the above results, located the nitrogen, oxygen, and one of the carbon atoms. Refinements of these atom positions followed by another Fourier synthesis revealed the remaining nonhydrogen atoms. One cycle of isotropic refinement yielded $R_1 = 0.093$ and $R_2 = 0.108$. At this point the absorption correction was applied to the data and two additional cycles gave $R_1 = 0.061$ and $R_2 = 0.075$. The 13 nonhydrogen atoms were refined with anisotropic temperature factors (including the real and imaginary dispersion correction[9] to the scattering factors of nickel and iodine), reducing R_1 to 0.049 and R_2 to 0.060. A difference Fourier map at this point exhibited maxima at reason-

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(8) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$ where $w = \sigma(F_o)^{-2}$.

(9) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

TABLE II

FRACTIONAL ATOMIC COORDINATES[a]

Atom	*x*	*y*	*z*
Ni	0[b]	0[b]	0[b]
I	0.21686 (13)	0.06119 (5)	0.29303 (10)
O	−0.0141 (15)	0.3754 (7)	0.4108 (10)
N	0.2068 (18)	0.5081 (10)	0.3906 (16)
C(1)	−0.2696 (19)	0.1537 (9)	0.0556 (16)
C(2)	−0.1288 (21)	0.1878 (9)	−0.0240 (16)
C(3)	−0.1048 (28)	0.2722 (11)	−0.0456 (19)
C(4)	−0.2228 (39)	0.3257 (12)	0.0063 (23)
C(5)	−0.3724 (34)	0.3055 (16)	0.0714 (27)
C(6)	−0.3965 (22)	0.2173 (14)	0.0990 (19)
C(7)	−0.2963 (25)	0.0706 (11)	0.1124 (20)
C(8)	0.2278 (21)	0.0755 (9)	−0.2047 (18)
C(9)	0.1442 (24)	0.1496 (12)	−0.1337 (20)
HC(3)	0.048	0.285	−0.063
HC(4)	−0.199	0.392	−0.011
HC(5)	−0.454	0.353	0.099
HC(6)	−0.494	0.185	0.158
HC(7)	−0.403	0.052	0.186
H(1)C(8)	0.360	0.049	−0.179
H(2)C(8)	0.182	0.090	−0.349
H(1)C(9)	0.226	0.167	0.006
H(2)C(9)	0.191	0.210	−0.218

[a] Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant digit(s). [b] Special position fixed by symmetry.

TABLE III

THERMAL PARAMETERS FOR $Ni(C_{18}H_{18}N_2O_2)I_2$[a]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Ni	152 (7)	29 (1)	153 (5)	2 (3)	57 (5)	5 (2)
I	184 (2)	49 (1)	146 (2)	−9 (1)	18 (1)	0 (1)
O	298 (30)	73 (6)	125 (16)	21 (12)	3 (18)	−17 (9)
N	198 (32)	68 (9)	219 (26)	−6 (13)	40 (23)	28 (13)
C(1)	158 (32)	43 (8)	137 (23)	10 (13)	−7 (23)	−15 (11)
C(2)	225 (38)	41 (8)	119 (23)	13 (14)	−30 (25)	−8 (11)
C(3)	379 (57)	49 (10)	195 (32)	−24 (20)	−83 (35)	−1 (14)
C(4)	560 (85)	52 (10)	212 (37)	85 (27)	−87 (46)	−25 (16)
C(5)	347 (62)	99 (16)	302 (47)	130 (29)	−31 (44)	−65 (23)
C(6)	165 (39)	100 (13)	179 (29)	−1 (19)	−2 (27)	−33 (17)
C(7)	275 (47)	48 (9)	227 (34)	−38 (17)	−52 (33)	−9 (15)
C(8)	254 (39)	50 (8)	204 (28)	−13 (15)	128 (29)	28 (13)
C(9)	213 (40)	99 (13)	222 (32)	−2 (19)	102 (30)	22 (17)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

able positions for the nine hydrogen atoms as well as a number of spurious peaks of comparable height. The hydrogen atoms were refined independently of the other atoms with isotropic temperature factors (hydrogen atoms attached to C(4) and C(5) did not refine to reasonable positions and were entered at the computed positions 1 Å from their respective carbon atoms for subsequent calculations). A final four cycles of least-squares refinement with the hydrogen atoms fixed and assigned temperature factors $B = 7.3$ Å^2 ($\sim$1 unit larger than the isotropic B of the carbon atoms) yielded final residuals $R_1 = 0.047$ and $R_2 = 0.058$. The standard deviation of an observation of unit weight was 1.83. In the final refinement cycle the largest parameter shift was less than 0.13 standard deviation. A final difference Fourier map showed no peaks larger than 0.55 e$^-$/Å^3 except near the iodine atom where peaks of 1.1 e$^-$/Å^3 appeared. Throughout the refinements, scattering factors for the neutral atoms were used as found in ref 10, while those for hydrogen were taken from Stewart, *et al.*[11] The observed and calculated structure factors are given in Table I. On the same scale, $F_c(000) = 570$. The final atomic positional parameters are listed in Table II and the components of the anisotropic thermal tensors for the nonhydrogen atoms are given in Table III.

Description and Discussion of the Structure

The structure consists of discrete molecules of $Ni(C_{18}H_{18}N_2O_2)I_2$ with the nickel atom at a center of symmetry. The nickel atom and the nitrogen and oxygen donor atoms of the macrocyclic ligand are thus required to be accurately coplanar. The iodine atoms are coordinated and lie above and below the Ni–O–N coordination plane on an axis that makes an angle of 88.9° with the Ni–O bond and 89.8° with the Ni–N bond. The least-squares plane through the benzo groups makes an angle of 14.6° with the coordination plane. A plan view of the molecule is given in Figure 1 (the iodine atoms are not shown) and the atom labeling scheme is indicated. Table IV gives selected bond distances and angles. A stereoview of the molecule illustrating the thermal ellipsoids is given by Figure 2. A stereoscopic packing diagram is provided by Figure 3.

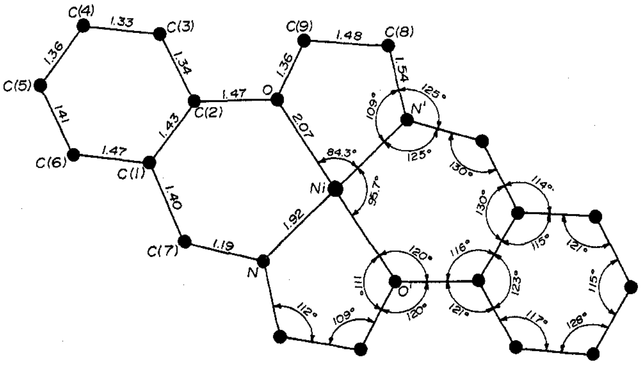

Figure 1.—Plan view of $Ni(C_{18}H_{18}N_2O_2)I_2$; the iodine atoms are not shown.

The Ni–I bond distance of 2.880 (3) Å is, as expected, longer than both a tetrahedral Ni^{II}–I distance of 2.55 Å[12] and five-coordinate distances of between 2.567 and 2.514 Å.[13] It is also significantly longer than the 2.67-Å distance calculated from the sum of covalent

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(10) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 201 ff.

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

(12) R. P. Taylor, D. H. Templeton, A. Zalkin, and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **7**, 2629 (1968).

(13) D. W. Meek and J. A. Ibers, *ibid.*, **8**, 1915 (1969).

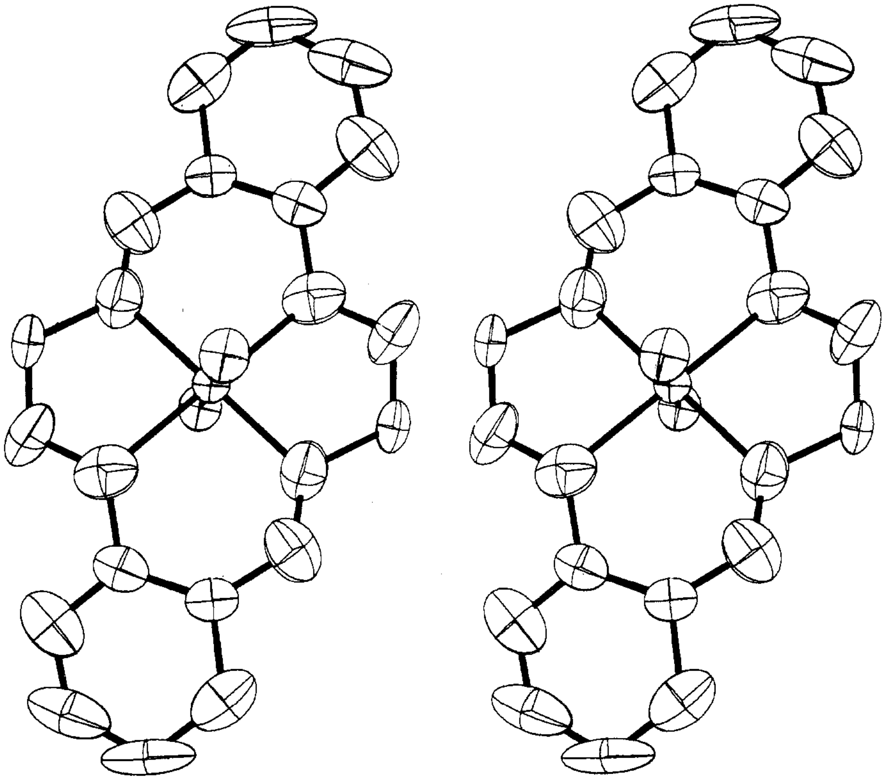

Figure 2.—Stereoview of $Ni(C_{18}H_{18}N_2O_2)I_2$. The atom labeling can be determined from Figure 1.

Table IV

Selected Bond Distances and Angles of $Ni(C_{18}H_{18}N_2O_2)I_2$

	Distances, Å		
Ni–I	2.880 (3)	C(1)–C(7)	1.40 (2)
Ni–O	2.07 (1)	C(1)–C(2)	1.43 (2)
Ni–N	1.92 (1)	C(2)–C(3)	1.34 (2)
C(7)–N	1.19 (2)	C(3)–C(4)	1.33 (3)
C(8)–N	1.54 (2)	C(4)–C(5)	1.36 (4)
C(9)–O	1.36 (2)	C(5)–C(6)	1.41 (3)
C(2)–O	1.47 (2)	C(6)–C(1)	1.46 (2)
C(8)–C(9)	1.48 (2)		
	Angles, Deg		
I–Ni–O	88.9 (3)	C(2)–C(1)–C(6)	115 (1)
I–Ni–N	89.8 (4)	C(2)–C(1)–C(7)	130 (1)
O–Ni–N	95.7 (5)	C(6)–C(1)–C(7)	114 (1)
O–Ni–N′	84.3 (5)	C(1)–C(2)–C(3)	123 (1)
Ni–O–C(2)	120.2 (8)	O–C(2)–C(1)	116 (1)
Ni–O–C(9)	111 (1)	O–C(2)–C(3)	121 (1)
C(2)–O–C(9)	120 (1)	C(2)–C(3)–C(4)	117 (2)
Ni–N–C(7)	125 (1)	C(3)–C(4)–C(5)	128 (2)
Ni–N–C(8)	109 (1)	C(4)–C(5)–C(6)	115 (2)
C(7)–N–C(8)	126 (1)	C(1)–C(6)–C(5)	121 (2)
N–C(8)–C(9)	112 (1)	N–C(7)–C(1)	130 (2)
O–C(9)–C(8)	109 (1)		

radii (octahedral Ni(II), 1.39 Å; I, 1.28 Å).[14] The present Ni–I distance agrees quite well with the 2.903 (7) Å apical Ni–I bond length in paramagnetic Ni(TAAB)$I_2 \cdot H_2O$[2,3] and, as expected, is much shorter than the 3.215 (2) Å[15] found in the strongly tetragonally distorted octahedral bis(*o*-phenylenebisdimethylarsine)nickel(II) iodide which is diamagnetic.

The Ni–N distance of 1.92 (1) Å is shorter than that in high-spin octahedral bis(*N*-γ-dimethylaminopropylsalicylaldiminato)nickel(II) (2.05 Å).[16] It compares well with this distance in low-spin Ni(TAAB)$(BF_4)_2$[2] and in the low-spin 14-membered-ring macrocyclic complex Ni-(*cis*-tetene)$(ClO_4)_2$.[4a] Since the macrocycle TAAB contains a 16-membered ring and the present ligand is comprised of only 14 member atoms, it may be that the constraint imposed by the shorter macrocyclic ring causes diminished nickel–donor atom distances in the present molecule.

The Ni–O distance of 2.07 (1) Å is slightly longer than found for the bound hydroxyl oxygen of salicylaldmine chelates of nickel (2.01 Å),[16,17] as would be expected for a weaker ether oxygen donor. It does agree quite well with the sum of covalent radii, 2.05 Å (octahedral Ni(II), 1.39 Å; O, 0.66).[14] It is considerably shorter, however, than the ether oxygen to nickel bond of 2.32 (1) Å found in five-coordinate dibromo[1-(*o*-methoxyphenyl)-2,6-diazaoctane]nickel(II),[18] perhaps owing to the constraint of the macrocyclic ring.

Further indication of strain in the macrocyclic coordination system which consists of two five- and two six-membered chelate rings is provided by a C(2)–O–C(9) angle of 120 (1)° at the ether oxygen and the fact that the ether oxygen is forced to be 0.18 Å from the plane of the benzo group. Likewise the imine carbon C(7) lies 0.25 Å on the side of the benzo plane opposite the oxygen and essentially in the Ni–O–N coordination plane (0.01 Å away).

The O–C(9)–C(8)–N chain, which forms a five-

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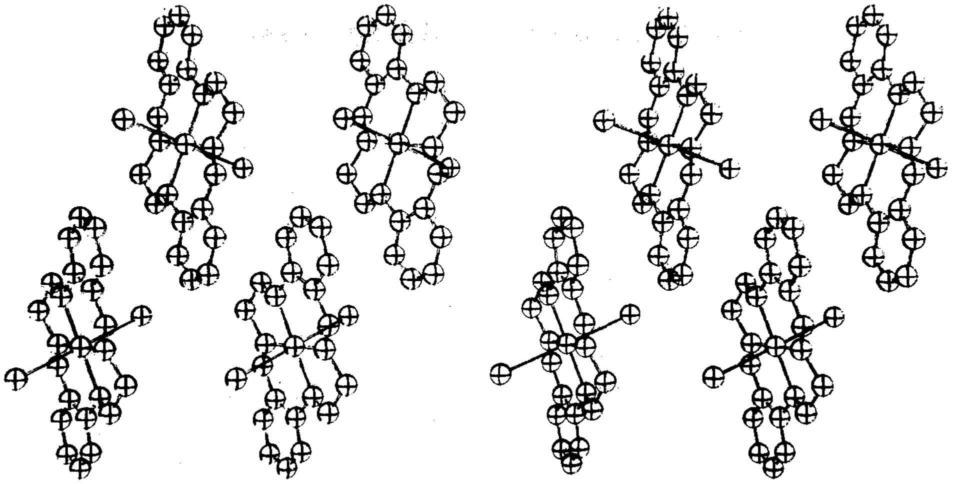

Figure 3.—Stereoscopic packing diagram showing the contents of two unit cells (stacked along the *c* direction) viewed down the a^* reciprocal axis with the *c* axis horizontal.

membered chelate ring with the nickel atom, is puckered. The carbon atom C(9) lies 0.40 Å on one side of the Ni–O–N coordination plane while C(8) is only 0.11 Å from this plane on the opposite side, as might be expected considering the idealized hybridizations of the oxygen (sp^3) and nitrogen (sp^2) donor atoms.

The benzo rings are unremarkable and are quite accurately planar with all atoms within 0.03 Å of the least-squares plane. The C–C bonds of the benzo group average 1.39 Å but exhibit sizable deviations from this mean value as has been found in other salicylaldimine chelates.[17] The present bond distances may suffer to some extent from greater inaccuracies owing to the presence of the heavy iodine atom which dominates the X-ray scattering.

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The Crystal Structure of Ba_2MnSe_3. Linear Antiferromagnetism in Ba_2MnX_3 (X = S, Se)[1]

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The compounds Ba_2MnSe_3 and Ba_2MnS_3 are isostructural with K_2AgI_3; the unit cell parameters for the selenide are a = 9.135 (2) Å, b = 4.471 (1) Å, and c = 17.736 (2) Å and for the sulfide a = 8.814 (5) Å, b = 4.302 (2) Å, and c = 17.048 (8) Å measured at 25 ± 0.5°, space group *Pnma*, $Z = 4$. Three-dimensional data were collected with Mo $K\alpha$ radiation, using balanced filters and the stationary-crystal, stationary-counter method to obtain peak heights. The structures were refined by least squares using anisotropic temperature factors to a final R value of 0.058 for 992 reflections for the selenide and to a final R value of 0.059 for 233 reflections for the sulfide using isotropic temperature factor parameters. The structure consists of $Mn-X_4$ tetrahedra sharing corners to produce infinite chains parallel to b. The magnetic susceptibility for both compounds was determined over the temperature interval 50–600°K by the Faraday technique. The Heisenberg model for a linear chain antiferromagnet and a "reduced-spin" model were used to calculate the exchange interaction parameter J/k and the Landé g factor. The results from both models are in close agreement with $J/k = -12.3$ (5)°K and g = 2.00 (3) for the sulfide and -9.8 (5)°K and g = 2.03 (3) for the selenide on the basis of the Heisenberg model.

Introduction

In the course of a study of the system BaX–M–X (X = S, Se; M = Mn, Fe, Co, Ni) we recently attempted to prepare $BaMnSe_2$ analogously to $BaNiS_2$ and $BaCoS_2$.[3] We were not able to prepare a single-phase material. The reaction mixture was found to consist of crystals of manganese selenide (α-MnSe) mixed with

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