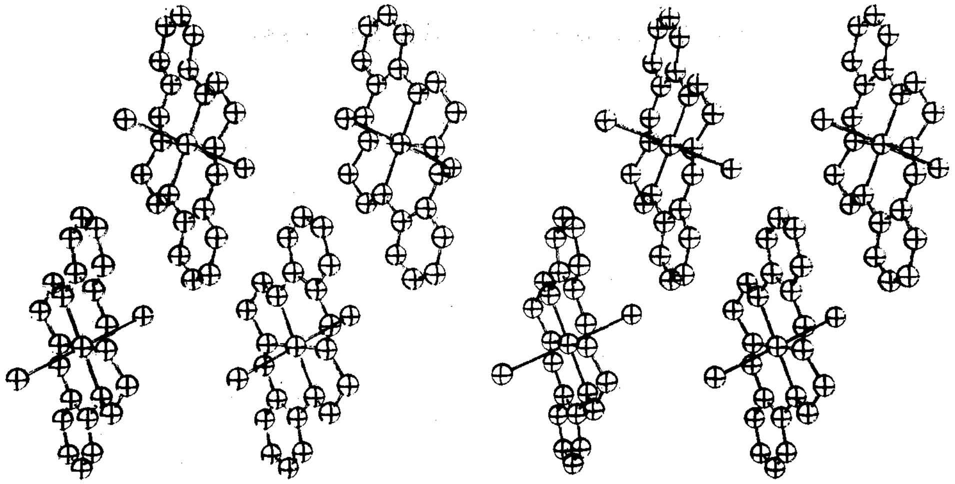

Figure 3.—Stereoscopic packing diagram showing the contents of two unit cells (stacked along the *c* direction) viewed down the a^* reciprocal axis with the *c* axis horizontal.

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 Kα 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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[1] Research sponsored by the Robert A. Welch Foundation, Houston, Texas.

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[3] I. E. Grey and H. Steinfink, *J. Amer. Chem. Soc.*, **92**, 5093 (1970).

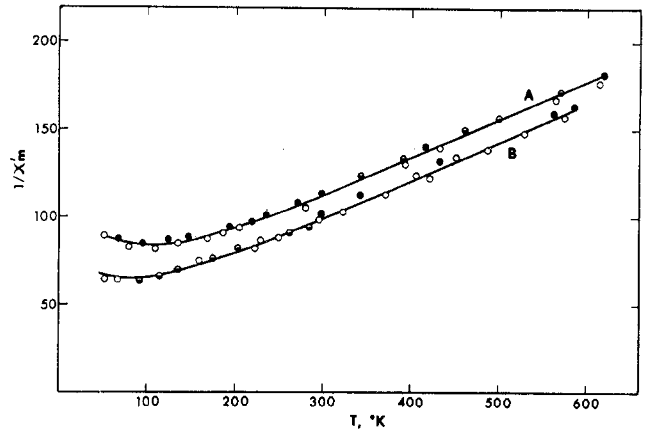

Figure 1.—Susceptibility data for Ba_2MnS_3 (A) and Ba_2MnSe_3 (B). The three sets of experimental points are results from three different preparations of A and B. The theoretical curve for A was calculated from eq 1 using $J/k = -12.3$°K, $g = 2.00$ and for B using $J/k = -9.8$°K, $g = 2.03$.

tabular orange crystals of an unknown phase.

A three-dimensional X-ray structural analysis showed that the composition was Ba_2MnSe_3. The compound has the K_2AgI_3 structure[4] so that manganese selenide tetrahedra share corners to produce infinite chains $[MnSe_2Se_{2/2}]_n^{4n-}$ parallel to the *b* axis. Neighboring chains are well separated and so the compound is a good example for studying linear antiferromagnetism in a chain composed of magnetic ions with five unpaired electrons. Divalent manganese, with a large spin, $S = {}^5/_2$, is particularly well suited to an application of the Heisenberg model linear chain antiferromagnet in the classical limit ($S \rightarrow \infty$) as developed by Fisher.[5] In the classical limit of infinite spin on the interacting ions, the quantum mechanical operators in the Heisenberg model may be replaced by classical vectors, allowing an exact solution. The model has been modified to apply to a Mn^{2+} system[6] resulting in a susceptibility expression

$$\frac{1}{\chi_m'} = \frac{0.937}{g^2}T\left[\frac{1 + \coth 17.5x - 0.0571/x}{1 - \coth 17.5x + 0.0571/x}\right] \qquad (1)$$

where g is the Landé factor, $x = -J/kT$, and J/k (in degrees Kelvin) is defined as negative for antiferromagnetic coupling.

Equation 1 has been used with some success in fitting susceptibility data for $[(CH_3)_4N]MnCl_3$[7] and $CsMnCl_3 \cdot 2H_2O$.[8] Theoretical analyses revealed that interchain interactions are many orders of magnitude smaller than intrachain exchange. For the latter compound corrections were made to account for the fact that the spin of manganese, although large, is not infinite as is formally required by the Fisher model. This correction was relatively minor, resulting in a change in the value of J of approximately 3%.

The compounds Ba_2MnX_3 (X = S, Se) are quite similar to $CsMnCl_3 \cdot 2H_2O$, with regard to the geometry of the Mn–X–Mn superexchange path and the Mn–Mn interchain and intrachain separations. We thus prepared pure samples of Ba_2MnSe_3 and the isomorphous Ba_2MnS_3 and carried out magnetic susceptibility measurements in the temperature range 50–600°K, to see how well the Fisher model applies to these compounds and to determine the effect of varying the covalency at the bridging ligand.

Experimental Section

(a) **Preparation.**—Attempts to prepare $BaMnSe_2$ were made by heating stoichiometric mixtures BaSe:Mn:Se in sealed Vycor tubes at temperatures ranging from 500 to 950°. In each case, the product consisted of a mixture of black crystals (MnSe) together with orange tabular crystals, identified subsequently by single-crystal X-ray analysis as Ba_2MnSe_3.

Pure samples of Ba_2MnSe_3 and Ba_2MnS_3 were then prepared by allowing the appropriate stoichiometric mixtures to react at 850 and 1050°, respectively. The reaction mixtures were contained within carbon tubes to prevent reaction with the Vycor ampoule and after heating for 2–5 days the samples were slowly cooled to room temperature. The resulting products were highly crystalline and the crystals formed deep orange-red columns. The formation of single-phase material was confirmed by microscopic examination and X-ray powder diffraction methods.

(b) **Magnetic Measurements.**—The magnetic susceptibility of finely powered samples of the compounds was measured in the temperature range 50 (pumped solid nitrogen) to 600°K by the Faraday technique. The apparatus employed a 6-in. electromagnet fitted with 4-in. Faraday pole caps, together with a Cahn RG electrobalance, sensitive to 0.1 μg. Separate, evacuable sample chambers were used for high- and low-temperature measurements. The magnetic field strength was determined individually for the separate chambers in place, using $CoHg(SCN)_4$. The susceptibilities of the compounds were checked at a number of values of the field gradient (HdH/dz) between 1.4×10^6 and 10.5×10^6 kG^2 cm^{-1}. Temperature runs were made on three separately prepared samples of each of the compounds. The values of the susceptibilities from different runs were in agreement to 2–4%.

The experimental results are summarized in the plots of inverse susceptibility *vs.* temperature in Figure 1.

X-Ray Structure Determination

Zero and upper level Weissenberg photographs of single crystals selected from the "$BaMnSe_2$" reaction mixture showed diffraction symmetry *mmm* and the systematic absences were $0kl$, $k + l = 2n + 1$ and $hk0$, $h = 2n + 1$, consistent with the space groups *Pnma* and $Pna2_1$. A columnar crystal measuring 0.06 × 0.05 × 0.15 mm was selected and mounted along its long dimension (*b* axis) on a GE single-crystal orienter. Eighty reflections were carefully centered on the $K\alpha_1$ and $K\alpha_2$ components of molybdenum radiation (λ_1 0.70926 Å, λ_2 0.71354 Å) using a 1° takeoff angle and a 0.02° slit. These 2θ measurements were used in a least-squares refinement for the determination of the lattice parameters $a = 9.135$ (2) Å, $b = 4.471$ (1) Å, $c = 17.736$ (2) Å, at 25 ± 0.5°.

Three-dimensional data to $(\sin \theta)/\lambda = 0.703$ were collected with Mo $K\alpha$ radiation, a 5° takeoff angle, balanced filters, and the stationary-crystal, stationary-counter method. Peak heights were counted for 10 sec using a zirconium filter; then background was counted for 10 sec using an yttrium filter. A total of 1180 independent reflections were measured of which

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TABLE I

(a) Final Atomic Parameters and Their Standard Deviations in Parentheses ($\times 10^4$) for Ba_2MnSe_3[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ba_1	4190 (1)	$^1/_4$	7137 (0.9)	21 (1)	53 (7)	4 (0.4)	0	0	0
Ba_2	2589 (1)	$^1/_4$	4571 (0.9)	25 (1)	68 (7)	3 (0.4)	0	−1 (0.7)	0
Mn	3738 (4)	$^1/_4$	1331 (2)	16 (4)	93 (20)	3 (1)	0	3 (1)	0
Se_1	3172 (3)	$^1/_4$	2732 (1)	21 (3)	94 (13)	1 (0.7)	0	−1 (0.8)	0
Se_2	1241 (2)	$^1/_4$	722 (1)	14 (2)	79 (13)	3 (0.7)	0	−1 (1)	0
Se_3	9967 (3)	$^1/_4$	5989 (1)	20 (3)	52 (13)	4 (0.7)	0	−1 (1)	0

(b) Atomic Parameters and Isotropic Temperature Factors for Ba_2MnS_3. Numbers in Parentheses are the Standard Deviations

	x	y	z	B, Å^2
Ba_1	0.4182 (6)	$^1/_4$	0.7137 (2)	1.1 (1)
Ba_2	0.2617 (5)	$^1/_4$	0.4558 (3)	1.1 (1)
Mn	0.3748 (12)	$^1/_4$	0.1320 (6)	1.1 (3)
S_1	0.3186 (23)	$^1/_4$	0.2711 (10)	1.1 (5)
S_2	0.1293 (22)	$^1/_4$	0.0724 (11)	1.1 (5)
S_3	0.9986 (21)	$^1/_4$	0.5993 (10)	0.8 (4)

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

993 were considered observed. Lorentz and polarization corrections were applied and an absorption correction made (μ 295.1 cm^{-1}). The absorption factor ranged from 4.4 to 7.0. The equation

$$\sigma(F) = \frac{1}{2}\left\{K\frac{[1 + I_Y/I_{Zr}]}{[1 - I_Y/I_{Zr}]}\right\}^{1/2}$$

where I_Y and I_{Zr} are the number of counts with the Y and Zr filters and K is the product of the Lorentz, polarization, absorption, α splitting, and tube current corrections, was used to estimate the standard deviation of the observed structure factor.

The choice of the centrosymmetric space group, *Pnma*, was made on the basis of the statistical distribution of the structure factors obtained from a Wilson plot calculation which also supplied approximate scale and temperature factors. The symbolic addition method for the direct determination of phases was used in the solution of the structure. The sequence of computer programs FAME–MAGIC–LINK–SYMPL[9] was used to generate 136 phases from which an E map was calculated showing clearly three selenium and two barium atoms. The E map was complicated by a pseudomirror plane at $x = 0.25$ but the correct set of atom positions was determined from packing considerations.

From a structure factor calculation based on the barium and selenium positions a discrepancy value, R, of 0.22 was obtained. A Fourier map revealed the position of the manganese atom. The atom parameters, scale, and isotropic temperature factors were then refined using a least-squares program XFLS, a modification of ORFLS.[10] The refinement was based on F_o and the structure factors were weighted by $1/\sigma^2$. After four cycles of refinement the value of R was 0.082. At this stage the isotropic temperature factors were converted to anisotropic factors and three more cycles of refinement led to a final R value of 0.070 for all measured reflections, with $R = 0.058$ and $wR = 0.069$ for nonzero reflections only. Atomic scattering factors were taken from ref 11 and were corrected for $\Delta f'$ and $\Delta f''$. The standard deviation of an observation of unit weight was 1.55. A three-dimensional difference map was calculated and showed no peaks greater than 0.5 e$^-$/Å^3.

The final positional parameters and anisotropic temperature factors are given in Table I. The bond distances and angles are given in Table II and Table III lists the F_o and F_c values.

TABLE II

BOND DISTANCES AND ANGLES IN Ba_2MnSe_3

	Distances, Å		
Mn–Mn(intrachain)	4.471 (1)	Ba_1–Se_1(2)	3.295 (4)
Mn–Mn(interchain)	6.164 (6)	Ba_1–Se_1(2)	3.282 (4)
		Ba_1–Se_2(2)	3.382 (4)
Mn–Se_1(1)	2.538 (6)	Ba_1–Se_3(1)	3.399 (4)
Mn–Se_2(1)	2.524 (6)		
Mn–Se_3(2)	2.601 (6)	Ba_2–Se_1(1)	3.304 (4)
		Ba_2–Se_2(1)	3.376 (4)
Se_1–Se_2(1)	3.978 (5)	Ba_2–Se_2(2)	3.211 (4)
Se_3–Se_3(1)	4.471	Ba_2–Se_3(1)	3.473 (4)
Se_1–Se_3(2)	4.177 (5)	Ba_2–Se_3(2)	3.382 (4)
Se_2–Se_3(2)	4.150 (5)		
	Angles, Deg		
Se_1–Mn–Se_2(1)	103.6 (2)	Se_1–Mn–Se_3(2)	108.7 (2)
Se_3–Mn–Se_3(1)	118.5 (2)	Se_2–Mn–Se_3(2)	108.1 (2)

X-Ray powder diffractograms for the corresponding sulfide, Ba_2MnS_3, were closely similar to those of Ba_2MnSe_3 and indicated that they are isostructural. Unit cell parameters were determined from a least-squares fit to the 2θ values for 15 nonoverlapping powder diffraction lines, obtained on a Philips powder diffractometer, using Cu Kα radiation, λ 1.542 Å, and are $a = 8.814$ (5), $b = 4.302$ (2), and $c = 17.048$ (8) Å, at 25 ± 0.5°. A single crystal of Ba_2MnS_3, whose largest dimension was approximately 50 μ, was mounted and three-dimensional reflection data to $2\theta = 40°$ were collected with Mo Kα radiation using the same experimental conditions as for Ba_2MnSe_3 and the reduction of the data was also the same. The coordinates ob-

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[10] W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn.

[11] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

TABLE III

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Ba_2MnSe_3[a]

H	L	FOBS	FCAL
***	K =	0	***
0	2	32	21
0	4	124	106
0	6	286	287
0	8	113	93
0	10	21	5*
0	12	254	246
0	14	124	116
0	16	191	191
0	18	100	93
0	20	30	33
0	22	112	121
0	24	60	64
1	1	19	7*
1	2	49	40
1	3	29	20
1	4	134	124
1	5	268	278
1	6	211	196
1	7	281	281
1	8	165	145
1	9	29	27
1	10	133	119
1	11	149	135
1	12	19	6*
1	13	134	120
1	14	25	18
1	15	95	84
1	16	244	249
1	17	16	12*
1	18	105	95
1	19	34	30
1	20	120	128
1	21	152	167
1	22	41	36
1	23	38	41
1	24	19	15*
2	0	60	54
2	1	69	60
2	2	155	148
2	3	22	3*
2	4	194	181
2	5	149	138
2	6	67	55
2	7	22	50
2	8	78	64
2	9	240	232
2	10	284	280
2	11	21	1*
2	12	127	114
2	13	62	60
2	14	94	89
2	15	123	114
2	16	45	33
2	17	16	5*
2	18	17	10*
2	19	41	46
2	20	33	27
2	21	79	83
2	22	106	111
2	23	107	126
2	24	50	48
3	1	170	163
3	2	267	296
3	3	19	13
3	4	67	55
3	5	68	55
3	6	315	335
3	7	234	227
3	8	66	56
3	9	87	75
3	10	180	170
3	11	30	25
3	12	164	155
3	13	95	88
3	14	89	80
3	15	137	127
3	16	16	4*
3	17	29	23
3	18	115	115
3	19	25	20
3	20	18	10*
3	21	29	22
3	22	131	145
3	23	19	23*
3	24	55	61
4	0	20	1
4	1	247	264
4	2	197	197
4	3	175	164
4	4	45	37
4	5	175	163
4	6	19	4*
4	7	26	21
4	8	23	23
4	9	31	22
4	10	37	35
4	11	116	105
4	12	58	51
4	13	149	137
4	14	291	297
4	15	125	116
4	16	119	113
4	17	140	142
4	18	44	39
4	18	44	39
4	19	63	66
4	20	176	184
4	21	53	57
4	22	109	114
4	23	19	12*
5	1	92	82
5	2	137	130
5	3	56	51
5	4	264	271
5	5	66	56
5	6	17	2*
5	7	173	168
5	8	208	201
5	9	78	72
5	10	66	58
5	11	159	147
5	12	15	4*
5	13	31	24
5	14	115	107
5	15	45	39
5	16	45	42
5	17	104	98
5	18	25	14*
5	19	103	105
5	20	112	113
5	21	92	91
5	22	19	7*
5	22	19	7*
6	0	127	119
6	1	40	35
6	2	35	29
6	3	47	38
6	4	160	152
6	5	188	180
6	6	77	72
6	7	52	44
6	8	155	144
6	9	63	61
6	10	92	84
6	11	95	82
6	12	217	216
6	13	22	8*
6	14	53	47
6	15	24	18*
6	16	40	40
6	17	31	24
6	18	18	12*
6	19	49	47
6	20	38	31
6	21	39	22
6	22	20	15*
7	1	122	113
7	2	84	74
7	3	117	108
7	4	131	124
7	5	67	60
7	6	30	22
7	7	84	77
7	8	218	216
7	9	160	158
7	10	37	29
7	11	100	95
7	12	112	110
7	13	68	63
7	14	94	91
7	15	66	63
7	16	104	100
7	17	75	79
7	18	112	113
7	19	109	111
7	20	71	71
8	0	150	152
8	1	96	88
8	2	261	269
8	3	130	123
8	4	168	157
8	5	14	4*
8	6	55	53
8	7	41	42
8	8	65	62
8	9	59	56
8	10	89	84
8	11	50	48
8	12	16	9*
8	13	77	70
8	14	107	103
8	15	106	102
8	16	61	55
8	17	26	9
8	18	81	87
8	19	64	66
9	1	23	15
9	2	32	23
9	3	112	104
9	4	21	4*
9	5	22	15*
9	6	153	148
9	7	27	20
9	8	23	17*
9	9	156	148
9	10	77	73
9	11	17	12*
9	12	53	49
9	13	30	20*
9	14	59	57
9	15	53	53
9	16	46	44
9	17	27	10*
10	0	47	36
10	1	51	43
10	2	102	99
10	3	39	34
10	4	39	35
10	5	31	27
10	6	68	65
10	7	70	66
10	8	49	45
10	9	58	58
10	10	126	126
10	11	116	113
10	12	60	57
10	13	95	93
10	14	65	61
10	15	27	9
11	1	78	75
11	2	54	50
11	3	105	103
11	4	132	125
11	5	132	130
11	6	17	15*
11	7	18	15*
11	8	103	102
11	9	120	119
11	10	39	30
11	11	93	96
11	12	35	28
12	0	114	109
12	1	35	28
12	2	51	41
12	3	99	91
12	4	91	88
12	5	18	10*
12	6	32	26
12	7	47	46
12	8	30	17*
***	K =	1	***
0	1	42	27
0	3	229	239
0	5	209	194
0	7	182	164
0	9	251	247
0	11	211	200
0	13	114	99
0	15	145	138
0	17	83	82
0	19	24	5*
0	21	171	181
0	23	33	12*
1	1	120	109
1	2	78	60
1	3	70	62
1	4	242	270
1	5	249	266
1	6	97	83
1	7	199	188
1	8	48	37
1	9	63	55
1	10	178	164
1	11	239	237
1	12	73	65
1	13	99	88
1	14	117	159
1	15	191	189
1	16	96	91
1	17	26	17
1	18	49	50
1	19	120	118
1	20	62	66
1	21	63	63
1	22	99	103
1	23	117	127
1	24	57	63
2	0	222	242
2	1	248	286
2	2	256	280
2	3	106	95
2	4	125	114
2	5	240	259
2	6	39	32
2	7	37	32
2	8	139	129
2	9	30	22
2	10	59	48
2	11	141	131
2	12	228	226
2	13	15	55*
2	14	77	75
2	15	22	3*
2	16	134	134
2	17	226	240
2	18	82	83
2	19	73	72
2	20	28	11*
2	21	57	64
2	22	91	98
2	23	43	48
2	24	39	33
3	1	223	241
3	2	58	50
3	3	190	183*
3	4	25	17
3	5	173	169
3	6	232	229
3	7	64	57
3	8	33	26
3	9	225	228
3	10	21	7*
3	11	99	91
3	12	173	167
3	13	78	69
3	14	38	32
3	15	54	50
3	16	16	14*
3	17	74	69
3	18	87	88
3	19	105	108
3	20	29	22
3	21	121	130
3	22	60	59
3	23	27	15*
4	0	22	17*
4	1	57	49
4	2	75	67
4	3	165	157
4	4	19	11*
4	5	151	147
4	6	35	29
4	7	246	250
4	8	49	45
4	9	131	121
4	10	129	118
4	11	95	93
4	12	64	59
4	13	91	86
4	14	85	82
4	15	86	78
4	16	37	35
4	17	165	170
4	18	18	4*
4	19	74	70
4	20	37	36
4	21	27	26
4	22	77	88
4	23	46	46
5	1	219	227
5	2	173	169
5	3	46	43
5	4	128	117
5	5	30	23
5	6	104	97
5	8	175	170
5	9	96	91
5	10	234	231
5	11	147	140
5	12	24	18
5	13	93	83
5	14	46	45
5	15	57	53
5	16	76	68
5	17	59	43
5	18	134	140
5	19	29	38
5	20	19	6*
5	21	30	16*
5	22	28	24
6	0	148	137
6	1	124	115
6	2	44	42
6	3	294	328
6	4	98	88
6	5	30	25
6	6	132	125
6	7	77	72
6	8	123	116
6	9	65	63
6	10	21	12*
6	11	45	41
6	12	33	28
6	13	148	145
6	14	31	30
6	15	184	182
6	16	39	39
6	17	25	28
6	18	49	48
6	19	161	174
6	20	33	34
6	21	19	8*
7	1	47	46
7	2	98	93
7	3	91	87
7	4	30	20
7	5	65	62
7	6	69	64
7	7	14	0*
7	8	212	217
7	9	77	69
7	10	32	29
7	11	40	38
7	12	28	18*
7	13	170	172
7	14	67	67
7	15	65	64
7	16	68	63
7	17	73	69
7	18	56	62
7	19	119	123
7	20	108	112
8	0	103	102
8	1	56	52
8	2	32	30
8	3	112	106
8	4	80	74
8	5	91	86
8	6	15	2*
8	7	157	159
8	8	56	55
8	9	38	41
8	10	16	7*
8	11	23	17
8	12	110	108
8	13	162	166
8	14	39	40
8	15	25	20*
8	16	60	60
8	17	46	47*
8	18	36	32
8	19	36	32
9	1	15	11*
9	2	89	87
9	3	161	158
9	4	137	134
9	5	50	47
9	6	48	41
9	7	120	122
9	8	26	28
9	9	170	173
9	10	69	69
9	11	27	24
9	12	48	50
9	13	132	140
9	14	18	3*
9	15	70	77
9	16	19	14*
9	17	19	18*
10	0	98	92
10	1	59	58
10	2	132	123
10	3	99	97
10	4	98	94
10	5	67	65
10	6	86	92
10	7	34	33
10	8	54	56
10	9	17	3*
10	10	76	78
10	11	59	61
10	12	18	20*
10	13	18	1*
10	14	139	146
10	15	33	33*
11	1	123	129
11	2	17	4*
11	3	17	3*
11	4	17	23*
11	5	18	13*
11	6	119	127
11	7	82	85
11	8	31	37
11	9	18	13*
11	10	26	26
11	11	78	80
11	12	33	32
12	0	18	15*
12	1	96	103
12	2	57	61
12	3	18	17*
12	4	35	1*
12	5	26	24
12	6	19	22*
12	7	83	89
12	8	40	43
***	K =	2	***
0	2	31	16
0	4	102	89
0	6	246	237
0	8	90	82
0	10	14	1*
0	12	221	216
0	14	107	101
0	16	169	175
0	18	84	86
0	20	31	27
0	22	103	111
1	1	10	4*
1	2	33	27
1	3	26	20
1	4	110	102
1	5	228	227
1	6	170	159
1	7	235	233
1	8	136	126
1	9	29	25
1	10	115	104
1	11	128	122
1	12	23	5*
1	13	120	107
1	14	22	14*
1	15	83	77
1	16	218	224
1	17	27	12*
1	18	89	86
1	19	31	28
1	20	115	118
1	21	138	153
1	22	40	33
1	23	39	39
2	0	45	41
2	1	58	52
2	2	130	120
2	3	17	2*
2	4	153	147
2	5	117	110
2	6	52	47
2	7	47	40
2	8	59	55
2	9	204	198
2	10	240	247
2	11	21	3*
2	12	107	101
2	13	59	56
2	14	86	81
2	15	105	103
2	16	35	30
2	17	17	4*
2	18	18	9*
2	19	44	42
2	20	29	24
2	21	74	76
2	22	89	102
2	23	100	116
3	1	142	136
3	2	231	241
3	3	19	9*
3	4	52	46
3	5	55	49
3	6	266	289
3	7	195	192
3	8	58	50
3	9	70	67
3	10	149	149
3	11	26	21
3	12	143	137
3	13	81	78
3	14	77	72
3	15	117	115
3	16	17	3*
3	17	27	20
3	18	101	108
3	19	26	19*
3	20	18	9*
3	21	27	21
3	22	118	135
4	0	15	7*
4	1	218	224
4	2	169	168
4	3	145	140
4	4	29	27
4	5	146	141
4	6	22	3*
4	7	25	18
4	8	26	18
4	9	30	20
4	10	38	32
4	11	98	94
4	12	50	47
4	13	127	124
4	14	255	268
4	15	107	106
4	16	101	102
4	17	126	130
4	18	38	35
4	19	57	60
4	20	156	169
4	21	49	52
4	22	99	106*
5	1	80	73
5	2	116	110
5	3	52	47
5	4	235	238
5	5	55	50
5	6	13	4*
5	7	149	147
5	8	180	179
5	9	69	67
5	10	58	53
5	11	137	130
5	12	16	5*
5	13	31	22
5	14	100	96
5	15	42	35
5	16	43	41
5	17	89	90
5	18	18	14*
5	19	93	98
5	20	100	105
5	21	79	84
6	0	110	106
6	1	37	32
6	2	28	24
6	3	37	35
6	4	139	136
6	5	160	157
6	6	66	64
6	7	41	39
6	8	132	129
6	9	54	52
6	10	76	76
6	11	79	73
6	12	191	197
6	13	17	8*
6	14	46	44
6	15	25	16*
6	16	33	38
6	17	26	22
6	18	26	12*
6	19	43	42
6	20	36	28
7	1	106	101
7	2	69	64
7	3	103	95
7	4	117	112
7	5	61	55
7	6	23	20
7	7	74	72
7	8	188	195
7	9	143	143
7	10	34	25
7	11	83	86
7	12	100	99
7	13	55	57
7	14	83	83
7	15	56	58
7	16	89	93
7	17	68	73
7	18	98	103
7	19	99	103
8	0	130	135
8	1	84	80
8	2	228	242
8	3	114	112
8	4	145	140
8	5	15	3*
8	6	47	48
8	7	37	38
8	8	51	57
8	9	51	51
8	10	81	77
8	11	52	44
8	12	17	8*
8	13	64	65
8	14	88*	96
8	15	93	94
8	16	49	50
8	17	27	8*
9	1	15	14*
9	2	26	23
9	3	96	94
9	4	16	4*
9	5	16	14*
9	6	133	136
9	7	16	18*
9	8	17	14*
9	9	134	135
9	10	63	68
9	11	18	13*
9	12	42	43
9	13	44	19
9	14	51	52
9	15	46	48
10	0	38	33
10	1	43	41
10	2	93	91
10	3	33	31
10	4	34	33
10	5	24	22
10	6	59	59
10	7	57	61
10	8	37	42
10	9	49	52
10	10	107	117
10	11	98	104
10	12	51	52
10	13	81	87
11	1	67	69
11	2	46	45
11	3	91	95
11	4	114	116
11	5	115	120
11	6	18	13*
11	7	26	15
11	8	32	95*
11	9	32	109*
11	10	27	27
12	0	100	103
12	1	32	26
12	2	41	38
12	3	83	84
12	4	82	81
***	K =	3	***
0	1	22	7*
0	3	180	163
0	5	161	144
0	7	144	128
0	9	197	188
0	11	170	160
0	13	84	75
0	15	120	118
0	17	67	66
0	19	19	0*
0	21	138	152
1	1	87	81
1	2	52	46
1	3	43	40
1	4	194	193
1	5	196	190
1	6	79	69
1	7	152	138
1	8	34	26
1	9	45	42
1	10	133	126
1	11	193	191
1	12	60	53
1	13	77	72
1	14	94	87
1	15	149	151
1	16	77	76
1	17	26	16*
1	18	41	42
1	19	99	99
1	20	57	58
1	21	57	52
2	0	170	167
2	1	201	204
2	2	204	198
2	3	76	71
2	4	94	90
2	5	190	192
2	6	34	21
2	7	33	24
2	8	101	92
2	9	24	16*
2	10	48	41
2	11	108	106
2	12	181	179
2	13	52	44
2	14	65	62
2	15	18	2*
2	16	108	112
2	17	188	201
2	18	60	70
2	19	64	62
2	20	27	10*
2	21	52	54
3	1	177	173
3	2	41	34
3	3	145	141
3	4	23	15*
3	5	130	126
3	6	178	171
3	7	49	43
3	8	26	16*
3	9	182	182
3	10	22	9*
3	11	75	70
3	12	139	136
3	13	60	59
3	14	30	23
3	15	53	45
3	16	18	11*
3	17	59	58
3	18	70	73
3	19	85	90
3	20	19	18*
3	21	97	114
4	0	23	15*
4	1	43	32
4	2	56	53
4	3	124	116
4	4	14	7*
4	5	113	111
4	6	29	21
4	7	190	196
4	8	42	35
4	9	104	100
4	10	103	96
4	11	73	75
4	12	57	49
4	13	74	76
4	14	66	70
4	15	65	64
4	16	37	31
4	17	131	141
4	18	27	1*
4	19	64	59
4	20	34	29
5	1	175	174
5	2	134	131
5	3	42	36
5	4	88	90
5	5	25	22
5	6	80	81
5	7	79	80
5	8	140	140
5	9	78	73
5	10	185	185
5	11	116	115
5	12	17	14*
5	13	73	70
5	14	38	37
5	15	45	41
5	16	53	55
5	17	52	54
5	18	110	120
5	19	34	34
6	0	114	112
6	1	97	91
6	2	38	33
6	3	269	264
6	4	71	67
6	5	24	20
6	6	104	98
6	7	58	58
6	8	90	90
6	9	55	53
6	10	17	11*
6	11	36	35
6	12	24	20
6	13	118	122
6	14	31	24
6	15	148	155
6	16	35	33
6	17	27	25
6	18	41	40
7	1	42	41
7	2	81	78
7	3	70	69
7	4	26	19
7	5	52	50
7	6	55	51
7	7	16	2*
7	8	172	180
7	9	60	56
7	10	27	21
7	11	41	35
7	12	25	15*
7	13	140	143
7	14	58	56
7	15	56	54
7	16	57	54
7	17	60	59
8	0	86	86
8	1	42	42
8	2	31	26
8	3	82	82
8	4	66	62
8	5	72	74
8	6	17	1*
8	7	126	133
8	8	48	46
8	9	34	35
8	10	18	6*
8	11	18	12*
8	12	89	93
8	13	134	141
8	14	35	35
8	15	27	16*
9	1	16	7*
9	2	72	73
9	3	129	132
9	4	110	111
9	5	48	41
9	6	37	34
9	7	78	103
9	8	28	23*
9	9	139	147
9	10	55	55
9	11	18	19*
9	12	44	42
9	13	110	119
10	0	77	77
10	1	17	51*
10	2	107	105
10	3	76	82
10	4	81	79
10	5	54	56
10	6	73	75
10	7	29	28
10	8	26	46
10	9	32	3*
10	10	65	68
11	1	103	109
11	2	37	3*
11	3	18	2*
11	4	19	18*
11	5	19	13*
***	K =	4	***
0	0	407	469
0	2	26	10*
0	4	78	68
0	6	183	166
0	8	72	63
0	10	18	4*
0	12	168	161
0	14	74	71
0	16	130	138
0	18	66	68
1	1	14	2*
1	2	27	12*
1	3	25	18*
1	4	75	72
1	5	169	158
1	6	114	106
1	7	176	160
1	8	101	94
1	9	27	20
1	10	35	75
1	11	99	95
1	12	18	3*
1	13	83	77
1	14	19	7*
1	15	60	60
1	16	166	170
1	17	28	11*
1	18	67	66
1	19	32	25
2	0	31	25
2	1	44	43
2	2	91	85
2	3	15	1*
2	4	107	102
2	5	79	71
2	6	35	36
2	7	36	25
2	8	45	41
2	9	148	137
2	10	188	183
2	11	18	7*
2	12	75	76
2	13	43	47
2	14	66	64
2	15	82	81
2	16	31	25
2	17	20	1*
2	18	20	5*
3	1	104	98
3	2	171	163
3	3	15	2*
3	4	37	31
3	5	41	39
3	6	211	213
3	7	117	132
3	8	44	37
3	9	52	50
3	10	111	111
3	11	26	15*
3	12	105	101
3	13	58	54
3	14	61	55
3	15	81	87
3	16	19	0*
3	17	28	14*
3	18	80	90
4	0	14	15*
4	1	166	159
4	2	126	122
4	3	106	100
4	4	25	12
4	5	106	161
4	6	16	0*
4	7	17	12*
4	8	30	11*
4	9	28	16*
4	10	31	27
4	11	76	72
4	12	47	36
4	13	96	95
4	14	198	203
4	15	78	82
4	16	74	76
4	17	100	102
5	1	57	55
5	2	80	75
5	3	41	40
5	4	178	174
5	5	41	35
5	6	16	6*
5	7	110	108
5	8	136	134
5	9	54	56
5	10	44	39
5	11	95	94
5	12	19	5*
5	13	27	17*
5	14	77	73
5	15	34	26
5	16	47	37
6	0	85	83
6	1	31	25
6	2	22	15*
6	3	30	27
6	4	109	105
6	5	117	112
6	6	49	47
6	7	34	29
6	8	100	98
6	9	44	35
6	10	56	59
6	11	58	53
6	12	152	156
6	13	19	7*
6	14	39	36
6	15	20	10*
7	1	79	78
7	2	50	44
7	3	75	71
7	4	89	87
7	5	46	43
7	6	17	16*
7	7	64	60
7	8	143	149
7	9	104	109
7	10	26	19
7	11	66	66
7	12	70	73
7	13	39	44
8	0	98	100
8	1	65	62
8	2	180	184
8	3	90	87
8	4	107	104
8	5	18	2*
8	6	34	36
8	7	26	29
8	8	41	43
8	9	37	41
8	10	19	61*
8	11	41	36
9	1	33	10*
9	2	28	23
9	3	75	72
9	4	18	3*
9	5	37	13*
9	6	104	110
9	7	19	12*
9	8	33	8*
***	K =	5	***
0	1	19	6*
0	3	27	105*
0	5	102	96
0	7	96	92
0	9	138	130
0	11	116	111
0	13	48	46
0	15	88	92
1	1	58	59
1	2	36	32
1	3	29	25
1	4	136	129
1	5	132	124
1	6	56	54
1	7	93	93
1	8	28	13*
1	9	31	26
1	10	89	86
1	11	134	135
1	12	43	41
1	13	52	53
1	14	62	60
1	15	99	104
2	0	114	109
2	1	139	136
2	2	135	129
2	3	51	50
2	4	67	64
2	5	133	130
2	6	27	11*
2	7	27	18*
2	8	61	55
2	9	20	10*
2	10	40	31
2	11	79	76
2	12	127	124
2	13	38	33
2	14	51	47
3	1	114	112
3	2	24	23
3	3	103	100
3	4	18	12*
3	5	91	85
3	6	116	111
3	7	41	32
3	8	19	6*
3	9	132	130
3	10	20	8*
3	11	49	48
3	12	89	93
3	13	48	47
4	0	16	15*
4	1	23	16*
4	2	43	41
4	3	84	75
4	4	18	2*
4	5	74	78
4	6	26	12*
4	7	136	136
4	8	27	24*
4	9	68	71
4	10	73	70
4	11	50	52
4	12	41	38
4	13	59	59
5	1	121	118
5	2	92	91
5	3	18	26*
5	4	68	60
5	5	18	21*
5	6	62	60
5	7	58	59
5	8	97	100
5	9	48	50
5	10	28	128*
5	11	81	86
6	0	75	77
6	1	69	64
6	2	28	23
6	3	182	187
6	4	49	44
6	5	19	16*
6	6	69	65
6	7	30	41*
6	8	66	61
6	9	44	41
7	1	34	34
7	2	57	56
7	3	49	48
7	4	19	19*
7	5	38	37
7	6	38	36
***	K =	6	***
0	0	295	296
0	2	22	7*
0	4	54	48
0	6	112	104
1	1	19	2*
1	2	21	4*
1	3	30	15*
1	4	61	56
1	5	112	105
1	6	78	66
1	7	110	102
2	0	18	14*
2	1	35	33
2	2	59	60
2	3	21	6*
2	4	67	65
2	5	48	44
2	6	37	25*
3	1	61	62
3	2	112	105
3	3	20	1*
3	4	20	19*
0	0	0	0

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[a] Those marked with asterisks were not used in the refinement.

tained for the selenide were used as a basis for least-squares refinement with isotropic temperature factors, and a final discrepancy value, $R = 0.058$, for all reflections (233) was obtained. The atomic parameters are listed in Table I and bond distances and angles are given in Table IV; Table V lists F_o and $|F_c|$.

TABLE IV

BOND DISTANCES AND ANGLES IN Ba_2MnS_3

Distances, Å		Angles, deg	
Mn–Mn(intrachain)	4.30	S_1–Mn–S_2(1)	103.3 (9)
Mn–Mn(interchain)	5.96 (2)	S_3–Mn–S_3(1)	119.8 (9)
		S_1–Mn–S_3(2)	108.1 (9)
Mn–S_1(1)	2.42 (3)	S_2–Mn–S_3(2)	108.1 (9)
Mn–S_2(1)	2.39 (3)		
Mn–S_3(2)	2.48 (3)		
S_1–S_2(1)	3.78 (3)		
S_3–S_3(1)	4.30		
S_1–S_3(2)	3.97 (3)		
S_2–S_3(2)	3.95 (3)		

TABLE V

OBSERVED AND CALCULATED VALUES OF THE STRUCTURE FACTORS FOR Ba_2MnS_3

H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL	H	L	FOBS	FCAL
***	K =	0	***	5	8	180	170	3	12	68	55	2	8	64	61
0	2	34	21	5	9	106	102	3	13	104	97	2	9	141	136
0	4	120	112	5	11	64	59	4	0	80	62	2	10	183	181
0	6	155	145	6	0	177	189	4	1	21	21	2	11	52	42
0	8	77	78	6	3	25	27	4	2	124	123	3	1	58	55
0	10	48	45	6	5	131	122	4	3	58	51	3	2	193	198
0	12	261	258	6	7	61	58	4	4	35	31	3	3	44	40
0	14	62	67	6	8	110	104	4	5	186	184	3	4	24	19
1	1	33	4	6	9	29	22	4	7	191	181	3	6	240	235
1	2	33	22	7	1	99	103	4	8	25	23	3	7	95	93
1	3	48	35	7	2	27	21	4	9	41	38	3	8	37	27
1	4	210	202	7	3	71	66	4	10	111	107	3	10	149	143
1	5	230	222	7	4	124	130	4	11	62	49	4	1	156	157
1	6	168	161	7	5	78	73	4	12	64	54	4	2	169	166
1	7	233	226	7	6	58	52	5	1	183	190	4	3	89	92
1	8	174	169	***	K =	1	***	5	2	144	149	4	4	53	48
1	9	63	62	0	1	35	29	5	3	24	20	4	5	104	102
1	11	75	75	0	3	297	296	5	4	67	65	4	7	27	18
1	13	60	53	0	5	110	102	5	5	47	43	4	8	75	67
1	14	44	29	0	7	133	126	5	6	118	110	5	2	79	80
2	0	83	79	0	9	228	218	5	7	87	88	5	3	62	64
2	1	80	76	0	11	127	127	5	8	101	91	5	4	182	174
2	2	215	209	0	13	39	22	5	9	52	45	5	5	47	48
2	3	113	115	1	1	138	139	5	10	149	144	5	7	122	113
2	4	92	87	1	2	44	46	6	0	58	55	6	0	163	162
2	5	116	112	1	3	90	90	6	1	102	100	6	3	28	25
2	6	27	15	1	4	200	196	6	2	45	46	6	4	103	114
2	7	38	29	1	5	193	184	6	3	221	222	***	K =	3	***
2	8	77	72	1	6	85	81	6	4	77	78	0	1	25	29
2	9	167	165	1	7	189	180	6	5	27	36	0	3	170	195
2	10	217	212	1	8	59	62	6	6	61	52	0	5	65	70
2	11	56	48	1	9	32	27	6	7	82	79	0	7	90	92
2	12	76	71	1	10	138	132	6	8	86	83	1	1	81	96
2	13	51	53	1	11	170	163	7	1	69	70	1	2	36	32
2	14	114	110	1	12	59	58	7	2	28	26	1	3	55	58
3	1	79	74	1	13	83	80	7	3	70	63	1	4	111	129
3	2	259	253	1	14	57	51	7	4	84	83	1	5	108	121
3	3	50	51	2	0	259	253	***	K =	2	***	1	6	51	61
3	4	30	25	2	1	211	203	0	0	430	514	1	7	121	124
3	6	288	282	2	2	195	187	0	2	21	15	1	8	40	47
3	7	120	115	2	3	82	78	0	4	83	91	2	0	164	167
3	10	175	168	2	4	72	65	0	6	114	109	2	1	132	132
3	12	111	105	2	5	235	222	0	8	65	68	2	2	111	121
3	13	26	20	2	7	102	95	0	10	42	37	2	3	46	52
4	1	191	192	2	8	60	55	0	12	231	220	2	4	43	49
4	2	198	201	2	9	41	35	1	3	34	31	2	5	139	154
4	3	115	112	2	10	39	34	1	4	141	162	2	7	69	69
4	4	63	61	2	11	83	76	1	5	164	171	3	1	125	123
4	5	122	123	2	12	176	169	1	6	121	125	3	2	27	21
4	7	33	21	2	13	95	85	1	7	178	181	3	3	121	125
4	8	82	81	3	1	186	184	1	8	145	142	3	4	28	15
4	9	36	18	3	2	38	35	1	9	60	53	3	5	103	106
4	10	94	93	3	3	179	174	1	11	75	66	3	6	88	94
4	11	86	87	3	4	29	23	2	0	62	62	4	0	52	45
4	12	40	27	3	5	157	150	2	1	64	64	4	2	90	89
5	2	94	97	3	6	143	136	2	2	158	166	4	3	45	34
5	3	67	73	3	7	107	102	2	3	92	95	4	4	29	23
5	4	212	207	3	9	219	210	2	4	66	64				
5	5	56	57	3	10	36	13	2	5	85	86				
	7	138	132	3	11	84	79	2	7	24	22				

Discussion

The structure of Ba_2MnSe_3 is illustrated in the stereographic drawing in Figure 2. It consists of infinite linear chains of $[MnSe_2Se_{2/2}]_n^{4n-}$ corner-sharing tetrahedra, parallel to the *b* axis, with barium ions packing between the chains. The two crystallographically independent barium ions have seven selenium atoms as nearest neighbors although the shapes of the coordination polyhedra differ markedly. The Ba_1 ion is at the center of a trigonal prism of selenium ions with the seventh selenium ion projecting from the center of one of the rectangular faces of the prism. All seven selenium ions belong to two neighboring linear chains. The Ba_1–Se distances range from 3.282 (4) to 3.399 (4) Å. The second barium ion coordinates to selenium ions from four surrounding linear chains at distances ranging from 3.211 (4) to 3.473 (4) Å. Within a linear chain, the manganese ions are at the centers of distorted tetrahedra of selenium ions. The bonds to the selenium ions involved in the corner sharing, Mn–Se_3, of length 2.601 (6) Å, are slightly longer than the other two Mn–Se bonds, 2.524 (6) and 2.538 (6) Å. The latter two distances are equal within the accuracy of the experiment and they subtend almost equal angles with Mn–Se_3, which are close to the tetrahedral angle, 109.5°. However there is a considerable distortion of the bridging angle, Se_3–Mn–Se_3, and the angle involving the nonbridging seleniums, Se_1–Mn–Se_2, to 118.5 (2) and 103.6 (2)°, respectively. The local site symmetry for the manganese ions is very close to C_{2v}.

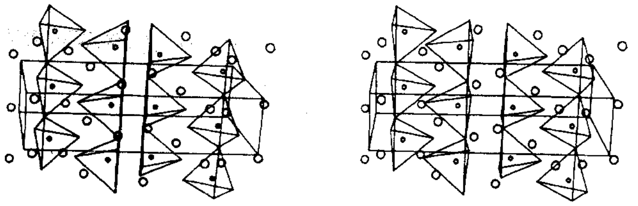

Figure 2.—Stereoscopic drawing of Ba_2MnSe_3. The unit cell outline is shown; the vertical axis is *b* and the horizontal axis is *c*. The structure is shown after a 15° rotation about *c*.

Within a linear chain the manganese ions are 4.471 Å apart whereas the shortest Mn–Mn separation between manganese ions in adjacent chains in 6.164 Å, the ions being separated by two selenium ions. Dominant magnetic interaction is expected within the linear chains, with only weak competing interchain interactions.

Equation 1 was applied in fitting the susceptibility data for Ba_2MnSe_3 and Ba_2MnS_3. The values of *g* and *J*/*k* were varied to obtain the best average fit of the theoretical curves to the susceptibility data for three separate preparations of each compound. The final values of *g* and *J*/*k* are given in Table VI and the re-

TABLE VI

MAGNETIC PARAMETERS FOR Ba_2MnS_3 AND Ba_2MnSe_3

Parameter	Ba_2MnS_3	Ba_2MnSe_3
μ_{eff} (300°K),[a] BM	4.65	4.90
Θ,[b] °K	210	150
J/*k*, °K (Heisenberg)	−12.3	−9.8
J/*k*, °K (reduced spin)	−11.5	−9.6
g (Heisenberg)	2.00	2.03
g (reduced spin)	1.98	2.02
g (exptl)	2.005	2.011

[a] $\mu_{eff} = 2.84\chi_m'T$. [b] Θ from $\chi_m' = C/(T + \Theta)$—extrapolation of high-temperature (>300°K) $1/\chi_m'$ *vs.* *T* data.

sulting theoretical curves are shown fitted to the experimental results in Figure 1. In view of the differences in susceptibilities for different sample preparations (2–4%) it was necessary to obtain an estimate of the errors associated with J/k and g. Values obtained from fitting eq 1 separately to the three sets of data differed up to 0.5°K in J/k and 0.03 in g and so these figures may be considered to be estimates of the errors associated with these quantities.

Also shown in Table VI are values of J/k and g obtained from application of the "reduced-spin" model, developed by Emori, *et al.*,[12] in which the susceptibility is given by

$$\chi_m' = \frac{Ng^2\beta^2S(S+1)}{3kT}\exp(J'/kT) \qquad (2)$$

and J' represents the exchange energy for a system composed of spins capable of orienting only parallel and antiparallel. The sign convention for antiferromagnetic exchange is negative in this theory. The true exchange integral, J/k, is given by

$$\frac{J}{k} = \frac{{}^3/_4 J'/k}{S(S+1)}$$

Figure 3 shows a plot of log $(3k/N\beta^2)\chi_m'T$ *vs.* $1/T$ from which g and J/k are obtained from the intercept $[=\log\{g^2S(S+1)\}]$ and the slope $[=J'/2.30k]$ of the straight line of best fit through the higher temperature (>120°K) results.

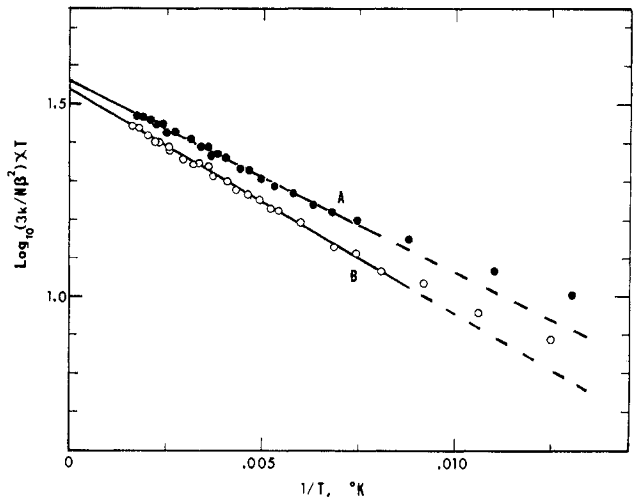

Figure 3.—Plot of susceptibility data using the "reduced-spin" model for (A) Ba_2MnSe_3 and (B) Ba_2MnS_3.

The fairly close agreement of the values of J/k and g with those obtained from the Heisenberg model indicates that eq 2 is a reasonable approximation for one-dimensional antiferromagnetics.

For comparison, experimental g values are also given in Table III. These were obtained from powder esr measurements on the compounds.[13]

The values of the exchange integral obtained for Ba_2MnS_3 and Ba_2MnSe_3 are considerably greater than those obtained for $CsMnCl_3 \cdot 2H_2O$ (J/k = −3.0°K) and reflect the greater superexchange capacity of the chalcogenides relative to the halides. The exchange integral J/k is a measure of the overall exchange energy resulting both from direct exchange between the metal atoms and from superexchange *via* the bridging ligands. For the compounds Ba_2MnX_3, the large intrachain Mn–Mn separation (~4.5 Å) is expected to exclude direct exchange and the exchange energy may be considered to result predominantly from exchange *via* the bridging chalcogenide.

The strengths of the various superexchange mechanisms possible between the half-filled Mn^{2+} d orbitals and the anion p orbitals depend both on the polarizability of the anions and the geometry of the bridging system, *i.e.*, on the Mn–X separation and on the Mn–X–Mn angle. One cannot predict, *a priori*, the variation in the exchange in going from the selenium to the sulfur compound on the basis of covalency alone, especially when the angles remain identical in the two compounds. The complexity of determining the various contributions to the sign and magnitude of the net exchange has been discussed by Konamori[14a] and by Huang and Orbach.[14b] Thus in the chromium chalcogenide spinels[14b] where antiferromagnetic interactions tend to increase from $O^{2-} \rightarrow S^{2-} \rightarrow Se^{2-}$ the effect is offset by an increase in the ferromagnetic interactions along this series and the net effect is not predictable. In the series $ZnCr_2Se_4 \rightarrow ZnCr_2S_4 \rightarrow ZnCr_2O_4$[15] the antiferromagnetic Curie–Weiss constant, Θ°K, becomes more negative so that the greater antiferromagnetic interaction in Ba_2MnS_3 is not unexpected although solely on the basis of the respective covalencies of the Mn–X bonds one would expect the superexchange to increase from the sulfide to the selenide. The value of Θ for Ba_2MnS_3 is also larger than for Ba_2MnSe_3.

We are studying the magnetic properties of the iron and cobalt compounds in order to gain further information concerning the exchange mechanisms present in these structures.

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[12] S. Emori, M. Inoue, M. Kishita, and M. Kubo, *Inorg. Chem.*, **8**, 1385 (1969).

[13] Esr measurements were carried out by Dr. R. W. Bene, Department of Electrical Engineering, University of Texas at Austin.

[14] (a) J. Konamori, *J. Phys. Chem. Solids*, **10**, 87 (1959); (b) N. Huang and R. Orbach, *J. Appl. Phys.*, **39**, 426 (1968).

[15] P. K. Baltzer, P. J. Wojtowicz, M. Robbins, and E. Lopatin, *Phys. Rev.*, **151**, 367 (1966).