Optical and Magnetic Studies of $CuSeO_3 \cdot 2H_2O$ Based on the Refined Crystal Structure

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(Received March 2, 1973)

Magnetic, IR and electronic spectral studies were made on $CuSeO_3 \cdot 2H_2O$, its crystal structure being refined. The IR band at 927 cm^{-1} was found to be due to a rocking vibration of a water molecule. The H-bonding scheme was suggested. The electronic spectrum shows a maximum of the d-d transition bands at *ca.* 14000 cm^{-1}. This was explained on the basis of a square pyramidal coordination of a Cu ion. Above 100 K the magnetic susceptibility obeys the Curie-Weiss law with $\theta = -92._6$ K and $\mu_{eff} = 2.00\ \beta_B$. At lower temperatures it shows a broad maximum at *ca.* 45 K, a sharp peak at $26._4$ K corresponding to T_N. The behaviour could be explained from the antiferromagnetic superexchange interactions of Cu cations through the σ-bonds of SeO_3^{2-} anions. The small anisotropy and the number of cations intermediated by each anion give rise to the 1-dimensional character. A linear Heisenberg model and the molecular field model gave J/k values of -33 and -31 K, respectively. The latter model also gave the observed ratio of $|\theta|/T_N$.

Magnetic properties of transition metal compounds have attracted the attention of many workers and studies have been carried out according to several different methods. The compounds studied can be classified into (a) those with highly anisotropic structures of a linear chain or a sheet arrangement of metal ions since the theories are expected to be phenomenologically applicable and (b) those in which the simple anions like halide or oxide anions coordinate to a metal atom since the quantum mechanics is useful for an explanation of the mechanism. They have given information on the nature of the chemical bond and the superexchange interaction. Studies on the compounds which belong to neither (a) or (b) do not seem to have been carried out. They are desirable because of their utility for testing the theories. The present study has been carried out with $CuSeO_3 \cdot 2H_2O$, the easiest system for application to the theory. The trigonal-pyramidal oxo-anion SeO_3^{2-} is potential to form MO's of both a σ- and a π-type character with metal cations. However, the nature of the bonds and the mechanism of magnetic interactions depend to a great extent on the conformation attained in the crystal lattice.

Experimental

Preparation. The hydrated sample was obtained by the usual method[1] and was confirmed by powder X-ray diffractometry[2] and also by chemical analysis of Cu content. A deuterated sample for IR study was obtained in a sealed tube at 120 °C with fully dried $CuSO_4$ and Na_2SeO_3 dissolved into D_2O. The powder X-ray diffraction pattern of the deuterate was the same as that of the hydrate.

IR and Electronic Spectra. IR spectra were recorded in the region 4000—400 cm^{-1} on a JASCO DS-402G spectrometer. Both KBr pellets and nujol mulls were employed. Diffuse reflectance spectra were obtained in the range 8250—35000 cm^{-1} with Hitachi EPU-2 and EPS-3T spectrometers with MgO as a standard. The spectra were recorded on a pure sample and one diluted with MgO to 80 wt.-%. Dilution was confirmed to have no effect on the position of absorption maxima.

Magnetic Measurement. Magnetic susceptibility was measured on powder samples by a Faraday balance. Temperatures were varied from 4 K to room temperature. $CoHg(SCN)_4$ was used as a reference substance of susceptibility.[3] Corrections were made for diamagnetism[4] but not for TIP.

Refinement of the Crystal Structure. The space group and lattice constants of Gattow[2] were confirmed; the space group is D_4^2-$P2_12_12_1$(No. 19) and lattice constants are $a = 6.664$, $b = 9.156$ and $c = 7.369(\pm 0.005)$ Å with $Z = 4$. Intensity data were collected using a Rigaku Denki four-circle X-ray diffractometer with a scintillation counter and Mo$K\alpha$ radiation. A total of 2311 reflections in two octants were measured within $\sin\theta/\lambda$ of 0.85. By averaging intensities of symmetry-related reflections in two octants,[5] intensities for 1347 independent reflections were obtained, of which 75 reflections had less than 2σ, the e.s.d. of $|F_o|$, and were taken to be zero. Intensities were corrected for Lorentz and polarization effects, but not for absorption and extinction effects. Dimensions of the crystal were $0.05 \times 0.08 \times 0.12$ mm^3; $\mu R = 1.19$.

Using atomic parameters of Gattow's analysis[2] and isotropic temperature factors of 1.0 for all atoms[6] as initial parameters, four cycles of the least-squares refinements were carried out. Anisotropic temperature factors were then introduced and four more cycles were repeated. Shifts of atomic parameters and temperature factors in the last cycle were less than 0.1 σ and 0.2 σ, respectively, with the exception of y-parameter of $O_w1(0.14\sigma)$ and a temperature factor $B12$ of $Cu(0.52\sigma)$. The final R-value $(R = \sum||F_o| - |F_c||\sum|F_o|)$ was 0.045 (0.038 excluding $|F_o| = 0$). In the earlier stages the weights were 1.0 for all reflections. In the later stages the following weights were used.

If $|F_o| \leqq 8.9$, $w = 0.25$,
if $|F_o| > 83.3$, $w = 1/|F_o|$,
and otherwise, $w = 1.0$.

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[1] Gmelins Handbuch der Anorganischen Chemie, Nr. 60, Cu, **B1**, 609 (1958).

[2] G. Gattow, *Acta Crystallogr.*, **11**, 377 (1958).

[3] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, **1958**, 4190.

[4] P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, New York (1956).

[5] Since this space group lacks the center of symmetry, 2311 reflections were taken to be independent at first and refinements were performed including imaginary parts of the anomalous dispersion. The atomic parameters for the two sets of indexing were the same within the e. s. d., and their R values were 0.080 and 0.068. The difference in the intensities of I_{hkl} and $I_{h\bar{k}l}$ were therefore taken to be an error in measurement and the average values of I_{hkl} and $I_{h\bar{k}l}$ were used for the later work, which is reported here.

[6] Only the atomic parameters were taken because of negative temperature factors.

Atomic scattering amplitudes used in these calculations were those of Cu^+, Se and O^-.[7] Corrections for the real parts of the anomalous dispersion were included. All calculations were performed with the aid of UNICS PROGRAM HBLS-IV and RSDA-4 on NEAC 2200/500 and 700 computers at the Computer Center, Osaka University.

Results and Discussion

IR Spectra. IR spectra of $CuSeO_3 \cdot 2H_2O$ and the dideuterate are shown in Fig. 1. The spectrum of the hydrate is in good agreement with that published by Sathianandan *et al.*[8] They assigned the band at 927 cm^{-1} to a bending vibration of Cu–O–Se. Since this band disappeared on deuteration, hydrogen atoms should take part in it. It can be assigned to a rocking vibrational mode of a water molecule. The corresponding band of a deuterate is not obvious because of its overlap with Se–O stretching bands. If we take a new band at 659 cm^{-1} as a rocking mode of D_2O, it gives 0.71 for the frequency ratio $\nu(D_2O)/\nu(H_2O)$, which is comparable to the observed ratios of $\nu(OD)/\nu(OH)$ and $\delta(D_2O)/\delta(H_2O)$ (0.73—0.74). Since the rocking vibration of a water of crystallization often appears at 800—700 cm^{-1},[9] this is a rare example of its appearing at a higher frequency.

Electronic Spectrum. The spectrum shown in Fig. 2 presents a broad *d-d* transition band at *ca.* 14000 cm^{-1} and an intense charge transfer band above 25000 cm^{-1}. The *d-d* transition band has a maximum at 13500 cm^{-1} and a shoulder at 10500 cm^{-1}. It is resolved into three components if we assume a Gaussian line shape with a common half width (Table 1).

A copper(II) cation is in an almost regular square pyramid composed of five oxygen atoms with a slight rhombic distortion (*vide post*). This configuration lacks the center of symmetry, explaining the high intensity of the absorption band. In this C_{2v} environment the 3*d* orbital levels are all split, three transitions being symmetry-allowed. The transition of $d_{x^2-y^2} \leftarrow d_{xy}$ is still forbidden, but the vibronic mechanism can bring forth the band of this transition.

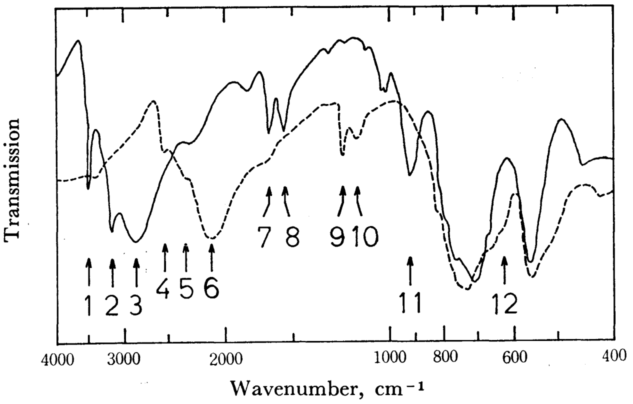

Fig. 1. Infrared spectra of $CuSeO_3 \cdot 2H_2O$ (——) and $CuSeO_3 \cdot 2D_2O$ (----). Bands attached with numbers are the vibrational modes involving H or D atoms.
1: ν_{OH}(3490 cm^{-1}), 2: ν_{OH}(3175 cm^{-1}), 3: ν_{OH}(2880 cm^{-1}), 4: ν_{OD}(2540 cm^{-1}), 5: ν_{OD}(2350 cm^{-1}), 6: ν_{OD}(2100 cm^{-1}), 7: δ_{HOH}(1650 cm^{-1}), 8: δ_{HOH}(1548 cm^{-1}), 9: δ_{DOD}(1215 cm^{-1}), 10: δ_{DOD}(1145 cm^{-1}), 11: $\nu_R(H_2O)$(927 cm^{-1}), 12: $\nu_R(D_2O)$(659 cm^{-1})

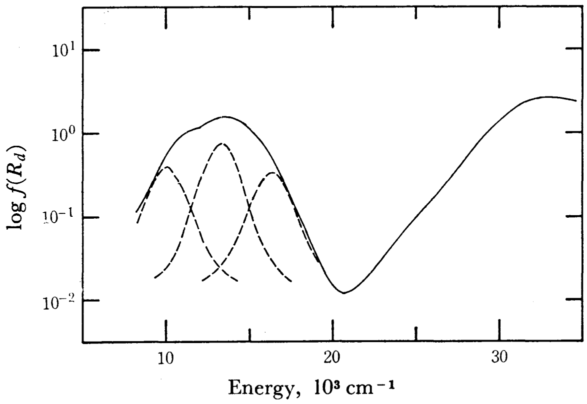

Fig. 2. Diffuse reflectance spectrum.
Observed (——) and resolved components (----).

Table 1. Resolution and assignment of the *d-d* transition bands

Energies (cm^{-1})	Relative intensity	Assignment[a]
10000	1.4	$^2A_1 \leftarrow {}^2A_2$
13200	1.7	$^2A_1 \leftarrow {}^2A_1'$
16300	1.3	$^2A_1 \leftarrow {}^2B_1, {}^2B_2$

a) Notations are given with an approximation of the C_{2v} point symmetry. A_1 and A_1' correspond to $d_{x^2-y^2}$ and d_{z^2} orbitals, respectively.

Since distortion is very small, it can be said that the energy difference between d_{xz} and d_{yz} orbitals is too small to be detected in the powder reflectance spectrum. Some polarized electronic spectra[10] show that this difference is less than 1500 cm^{-1} and that the transitions occur at 14200—16800 cm^{-1}. The component at 16300 cm^{-1} can therefore be assigned to the $d_{x^2-y^2} \leftarrow d_{xz}, d_{yz}$ transitions. This is also confirmed in the following estimation.

Copper(II) complexes in an environment of a tetragonally distorted octahedron of oxygen atoms give transitions of $d_{x^2-y^2} \leftarrow d_{z^2}$ in a wide range of energy. This energy was shown to be related to the axial Cu–O bond length.[11] Smith[12] succeeded in explaining the relationship from the molecular orbital formation between copper and ligand atoms and the electrostatic crystal field energy. His treatment was modified[12,13] for a square pyramidal coordination with the C_{4v}

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[7] IUCr, "International Tables for Crystallography," Vol. 3, Kynoch Press, Birmingham (1962).

[8] K. Sathianandan, L. D. McCory and J. L. Margrave, *Spectrochim. Acta*, **20**, 957 (1964).

[9] H. J. Prask and H. Boutin, *J. Chem. Phys.*, **45**, 699, 3284 (1966).

[10] R. J. Dudley and B. J. Hathaway, *J. Chem. Soc. A*, **1970**, 1725; M. J. Bew, R. J. Dudley, R. J. Fereday, B. J. Hathaway and R. C. Slade, *ibid.*, **1971**, 1437; R. J. Dudley and B. J. Hathaway, *ibid.*, **1971**, 1442.

[11] D. E. Billing, B. J. Hathaway and P. Nichols, *ibid.*, **1969**, 316.

[12] D. W. Smith, *ibid.*, **1970**, 176.

[13] C. E. Schäffer and C. K. Jørgensen, *Mol. Phys.*, **9**, 401 (1965); D. W. Smith, *J. Chem. Soc. A*, **1969**, 1708.

symmetry, giving the energies 12900, 11400 and 15100-17600 cm^{-1} for $d_{x^2-y^2} \leftarrow d_{z^2}$, $d_{x^2-y^2} \leftarrow d_{xy}$ and $d_{x^2-y^2} \leftarrow d_{xz}, d_{yz}$, respectively. These values are in good agreement with those of resolved components. π-bonding between copper and basal oxygen atoms were involved in this estimation. Since these quantities were treated only as parameters to fit the data by Smith, the agreement between resolved and estimated values does not necessarily mean the presence of the π-bonding. It might be negligible in this compound.

Refined Crystal Structure. The final atomic parameters, temperature factors and $|F_o|$'s and $|F_c|$'s are given in Tables 2, 3 and 4, respectively. The projection of the refined structure to the (100) plane is shown in Fig. 3. Interatomic distances and angles are given in Table 5.

The gross feature of the structure is the same as that of Gattow,²⁾ but significant shifts (0.06—0.15 Å) of oxygen atoms were found. Thus the selenium and copper atoms attain more regular coordinations.

TABLE 2. POSITIONAL PARAMETERS
Values in parentheses are the e.s.d.'s in the last decimal.

Atom	x/a	y/b	z/c
Cu	0.4809(1)	0.6542(1)	0.2860(1)
Se	0.7287(1)	0.3911(1)	0.4573(1)
O 1	0.2556(7)	0.7812(5)	0.2283(6)
O 2	0.5288(6)	0.6137(5)	0.0295(6)
O 3	0.7335(7)	0.5594(5)	0.3561(6)
O_w 1	0.4489(7)	0.7155(5)	0.5425(7)
O_w 2	0.2921(8)	0.4415(6)	0.3100(8)

TABLE 3. TEMPERATURE FACTORS (× 10^4) IN THE FORM OF $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$
Values in parentheses are the e.s.d.'s in the last decimal.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	55(1)	30(1)	34(1)	22(2)	0(2)	−2(1)
Se	42(1)	24(0)	29(1)	0(1)	2(1)	−2(1)
O 1	64(8)	41(4)	52(6)	39(10)	46(3)	28(8)
O 2	57(7)	45(4)	37(5)	7(11)	−1(12)	−5(9)
O 3	64(8)	29(4)	64(6)	11(10)	−25(13)	7(8)
O_w 1	92(9)	53(5)	47(6)	41(11)	−5(15)	−10(10)
O_w 2	94(10)	66(8)	85(8)	30(13)	9(17)	0(12)

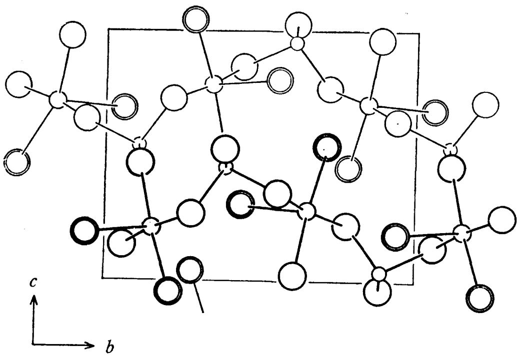

Fig. 3. Crystal structure of $CuSeO_3 \cdot 2H_2O$ projected to the (100) plane. The middle circle shows a Cu atom, the smallest one Se, the largest single one $O(SeO_3)$ and the largest double one $O(H_2O)$.

The bond lengths and angles show that the copper atom is located in the square pyramid of oxygen atoms rather than in the distorted octahedron as stated by Gattow²⁾ and Handlovič¹⁴⁾ for the isomorphous $CuHPO_3 \cdot 2H_2O$. Four oxygen atoms forming the basal plane are planar, the deviations being within 0.030 Å. The copper atom is 0.137 Å above this plane as is often the case in the copper complexes of a square pyramidal configuration. Three interatomic distances (mean 1.952 Å) of basal Cu-O(SeO_3) bonds are the same within the e.s.d., but the basal Cu-O_w1 distance is significantly longer. The apical Cu-O_w2 distance became longer than that of Gattow's structure (2.27→2.323 Å), whereas the next-nearest oxygen atom O_w2' came closer than before (3.21→3.117 Å). In spite of the shortened Cu-O_w2' distance this oxygen atom should be excluded from coordination to the copper atom, not only because it is much longer than the longest one in the square pyramid but also because the copper atom has three next-nearest neighbours of uncoordinating Se atoms at 3.128—3.182 Å. This configuration is in good agreement with that of $CuHPO_3 \cdot 2H_2O$,¹⁴⁾ $Cu(NH_3)_4SO_4 \cdot H_2O$¹⁵⁾ and $Cu(NO_3)_2 \cdot CH_3NO_2$.¹⁶⁾

A selenite anion forms a very slightly distorted trigonal pyramid. Its average dimensions are Se–O = 1.70_6, O–O = 2.60_7 Å and O-Se-O = 99.7° with the selenium atom 0.80_3 Å above the basal plane. These values are comparable to those of $ZnSeO_3 \cdot 2H_2O$,¹⁷⁾ $MgSeO_3 \cdot 6H_2O$,¹⁸⁾ H_2SeO_3,¹⁹⁾ $Na_3H(SeO_3)_2$²⁰⁾ and $K_3H(SeO_3)_2$.²¹⁾ A selenite anion coordinates to three different copper atoms, with each oxygen atom towards a single copper atom, and connects the CuO_5 pyramids into a three-dimensional network.

No hydrogen atoms could be found in the analysis. However, consideration of interatomic distances and angles around O_w1 and O_w2 led to the sole probable scheme of hydrogen bonds of water molecules. A water molecule H_2O 1 may direct its hydrogen atoms towards O 1 and O 3 belonging to the two neighbouring CuO_5 pyramids and its negative dipole towards the copper atom (Table 5). The water molecule H_2O 2 has two copper neighbours. The angle Cu-O_w2-Cu′ and also an electrostatic repulsion between hydrogen and copper atoms suggest a configuration in which two lone pairs direct towards two copper atoms and one hydrogen atom to O 2 atom belonging to another CuO_5 neighbour. Another hydrogen atom may be free from the hydrogen bonding or incorporated to

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15) B. Morosin, *ibid.*, **B25**, 19 (1969).

16) B. Duffin and S. C. Wallwork, *ibid.*, **20**, 210 (1966).

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20) S. F. Kaplan, M. I. Kay and B. Morosin, *Ferroelectrics*, **1**, 31 (1970).

21) M. S. Lehmann and F. K. Larsen, *Acta Chem. Scand.*, **25**, 3859 (1971).

TABLE 4. STRUCTURE FACTORS $3|F_o|$ AND $3|F_c|$

K	|FO|	|FC|
H = 0 L = 0		
2	70	59
4	436	439
6	50	41
8	127	122
10	16	18
12	40	21
14	40	38
H = 1 L = 0		
1	300	294
2	345	344
3	156	147
4	218	219
5	238	240
6	67	70
7	29	28
8	142	137
9	195	192
10	15	16
11	32	36
12	76	77
13	88	90
14	50	50
15	50	46
H = 2 L = 0		
0	145	127
1	144	125
2	256	232
3	0	1
4	32	8
5	83	80
6	325	321
7	41	38
8	59	55
9	11	13
10	194	189
11	25	21
12	87	85
13	19	9
14	96	96
15	23	6
H = 3 L = 0		
1	287	276
2	403	402
3	232	226
4	101	93
5	146	138
6	144	138
7	17	9
8	53	53
9	131	128
10	15	16
11	21	0
12	0	15
13	38	38
14	42	37
15	44	40
H = 4 L = 0		
0	564	569
1	28	33
2	23	27
3	92	85
4	294	288
5	0	2
6	16	13
7	137	138
8	92	91
9	35	39
10	17	10
11	98	100
12	19	7
13	42	42
14	26	32
H = 5 L = 0		
1	122	114
2	13	8
3	20	10
4	144	137
5	175	168
6	21	22
7	65	63
8	152	151
9	141	140
10	56	54
11	39	40
12	89	90
13	85	87
H = 6 L = 0		
0	70	61
1	174	166
2	56	53
3	82	77
4	17	11
5	131	124
6	152	149
7	77	73
8	43	41
9	31	25
10	113	108
11	36	34
12	60	58
13	22	22
H = 7 L = 0		
1	144	137
2	219	205
3	132	125
4	0	1
5	46	46
6	124	116
7	36	28
8	23	10
9	25	20
10	31	22
11	32	20
12	39	34
H = 8 L = 0		
0	139	133
1	0	9
2	17	10
3	82	78
4	90	87
5	26	13
6	0	6
7	135	131
8	31	28
9	47	46
10	0	0
11	111	113
H = 9 L = 0		
1	17	15
2	78	73
3	38	40
4	51	52
5	43	46
6	60	55
7	63	61
8	92	92
9	57	63
H =10 L = 0		
0	0	16
1	102	100
2	0	1
3	75	72
4	0	3
5	84	81
6	41	37
7	47	50
H =11 L = 0		
1	42	38
2	81	77
3	44	46
H = 0 L = 1		
1	143	146
2	157	156
3	365	351
4	159	149
5	75	68
6	92	88
7	272	261
8	223	213
9	34	28
10	69	68
11	158	154
12	89	87
13	67	61
14	48	46
15	66	73
H = 1 L = 1		
0	336	350
1	116	121
2	305	311
3	112	104
4	212	211
5	108	103
6	261	263
7	82	78
8	147	146
9	0	10
10	140	139
11	52	47
12	116	120
13	23	25
14	24	27
15	22	9
H = 2 L = 1		
0	0	4
1	256	259
2	351	356
3	156	154
4	156	158
5	89	89
6	117	114
7	162	161
8	88	86
9	35	39
10	28	29
11	96	95
12	39	35
13	52	49
14	59	56
15	30	27
H = 3 L = 1		
0	144	147
1	113	109
2	193	187
3	70	64
4	155	154
5	140	137
6	240	238
7	91	91
8	112	109
9	85	83
10	112	110
11	80	80
12	112	112
13	55	56
14	39	29
H = 4 L = 1		
0	217	212
1	123	122
2	111	111
3	210	206
4	159	150
5	42	41
6	68	66
7	188	188
8	157	159
9	25	26
10	78	78
11	118	117
12	68	70
13	47	44
14	47	46
H = 5 L = 1		
0	235	231
1	171	172
2	214	205
3	75	72
4	121	120
5	142	136
6	142	137
7	25	22
8	89	89
9	57	59
10	80	85
11	18	12
12	70	67
13	25	25
H = 6 L = 1		
0	70	71
1	90	91
2	145	140
3	116	111
4	126	121
5	62	61
6	84	79
7	104	103
8	62	59
9	65	66
10	64	60
11	52	52
12	35	22
13	54	56
H = 7 L = 1		
0	20	18
1	111	112
2	72	69
3	50	47
4	44	46
5	128	127
6	100	97
7	57	54
8	47	47
9	97	95
10	50	51
11	62	60
12	59	58
H = 8 L = 1		
0	166	158
1	80	77
2	43	41
3	101	94
4	124	119
5	0	18
6	52	50
7	77	77
8	81	83
9	27	17
10	57	59
H = 9 L = 1		
0	85	85
1	111	115
2	65	63
3	48	46
4	42	40
5	108	108
6	42	41
7	20	17
8	33	16
9	55	59
H =10 L = 1		
0	70	69
1	0	14
2	32	32
3	48	46
4	65	65
5	36	30
6	50	49
7	56	49
H =11 L = 1		
0	0	17
1	66	66
2	23	17
3	26	31
H = 0 L = 2		
0	20	15
1	306	309
2	113	115
3	116	118
4	125	116
5	134	128
6	262	260
7	38	37
8	135	133
9	0	2
10	232	226
11	0	4
12	83	80
13	20	6
14	112	113
15	26	26
H = 1 L = 2		
0	210	210
1	260	264
2	171	177
3	96	96
4	153	155
5	272	275
6	135	134
7	82	81
8	152	151
9	117	114
10	70	73
11	66	68
12	58	54
13	60	71
14	60	60
15	47	47
H = 2 L = 2		
0	262	278
1	171	168
2	45	44
3	49	51
4	342	360
5	141	143
6	99	99
7	109	108
8	121	117
9	113	112
10	0	11
11	41	42
12	28	32
13	69	67
14	43	49
15	24	21
H = 3 L = 2		
0	193	194
1	149	150
2	70	73
3	68	70
4	184	188
5	189	185
6	53	49
7	33	31
8	172	172
9	123	128
10	70	70
11	54	50
12	87	88
13	78	83
14	53	52
H = 4 L = 2		
0	0	6
1	201	207
2	103	105
3	196	197
4	80	82
5	114	118
6	180	180
7	70	65
8	108	111
9	31	32
10	151	155
11	21	10
12	69	70
13	0	18
14	82	85
H = 5 L = 2		
0	76	77
1	166	167
2	196	197
3	135	135
4	53	54
5	162	162
6	140	136
7	124	122
8	38	32
9	53	48
10	51	53
11	58	60
12	21	24
13	28	31
H = 6 L = 2		
0	179	178
1	43	44
2	91	89
3	66	67
4	159	157
5	98	94
6	95	91
7	99	98
8	45	48
9	73	71
10	25	21
11	78	76
12	28	30
H = 7 L = 2		
0	112	107
1	72	72
2	38	36
3	69	70
4	117	113
5	76	74
6	75	71
7	53	52
8	98	97
9	72	72
10	44	48
11	39	39
H = 8 L = 2		
0	0	13
1	135	130
2	50	52
3	134	134
4	38	38
5	89	86
6	65	66
7	58	59
8	63	64
9	34	28
10	52	53
H = 9 L = 2		
0	0	1
1	61	63
2	118	116
3	82	84
4	0	12
5	45	40
6	74	77
7	75	80
8	37	25
9	24	8
H =10 L = 2		
0	42	41
1	0	4
2	63	65
3	56	50
4	40	32
5	36	38
6	50	52
H =11 L = 2		
0	41	39
1	49	44
2	41	46
H = 0 L = 3		
1	244	244
2	320	331
3	294	294
4	79	80
5	206	204
6	209	204
7	106	104
8	27	22
9	41	40
10	32	29
11	28	27
12	35	32
13	37	38
14	34	34
15	22	22
H = 1 L = 3		
0	200	194
1	125	128
2	266	274
3	237	245
4	168	169
5	51	50
6	157	158
7	170	172
8	90	90
9	73	74
10	97	95
11	86	85
12	70	71
13	61	61
14	52	48
15	50	48
H = 2 L = 3		
0	60	64
1	96	97
2	29	26
3	116	118
4	194	200
5	95	96
6	126	128
7	147	150
8	161	165
9	66	65
10	63	62
11	113	113
12	133	134
13	24	21
14	46	45
H = 3 L = 3		
0	218	221
1	183	185
2	203	215
3	230	239
4	164	168
5	117	116
6	125	126
7	145	147
8	38	41
9	0	13
10	40	41
11	61	56
12	45	41
13	28	32
14	0	9
H = 4 L = 3		
0	81	80
1	173	176
2	216	221
3	186	186
4	46	45
5	143	147
6	164	169
7	72	73
8	32	38
9	57	55
10	63	68
11	30	32
12	36	37
13	48	50
14	45	44
H = 5 L = 3		
0	16	11
1	43	41
2	102	107
3	96	99
4	87	93
5	70	69
6	119	118
7	96	97
8	98	101
9	100	100
10	95	96
11	68	73
12	70	70
13	64	63
H = 6 L = 3		
0	117	121
1	133	132
2	19	15
3	130	130
4	133	134
5	88	88
6	47	50
7	86	86
8	95	95
9	43	42
10	37	36
11	51	54
12	70	69
H = 7 L = 3		
0	130	131
1	116	116
2	92	94
3	122	123
4	111	112
5	99	97
6	53	57
7	55	55
8	46	46
9	53	52
10	9	6
11	21	16
H = 8 L = 3		
0	47	46
1	66	68
2	72	74
3	60	62
4	36	38
5	78	79
6	90	91
7	38	37
8	45	45
9	60	62
10	65	70
H = 9 L = 3		
0	45	48
1	50	50
2	22	24
3	14	15
4	56	57
5	70	73
6	57	59
7	36	31
8	50	58
H =10 L = 3		
0	78	83
1	78	81
2	0	5
3	69	71
4	68	72
5	55	59
6	0	9
H = 0 L = 4		
0	334	345
1	21	23
2	105	103
3	81	85
4	196	192
5	214	212
6	28	29
7	40	37
8	92	92
9	191	188
10	22	21
11	80	76
12	20	4
13	121	119
14	28	17
H = 1 L = 4		
0	262	262
1	227	233
2	157	161
3	90	92
4	222	225
5	168	166
6	96	97
7	20	15
8	116	116
9	113	116
10	85	86
11	37	39
12	43	46
13	37	41
14	68	70
H = 2 L = 4		
0	60	58
1	239	242
2	43	41
3	271	280
4	76	76
5	158	157
6	117	120
7	124	123
8	62	64
9	83	87
10	110	111
11	0	20
12	48	51
13	0	23
14	43	49
H = 3 L = 4		
0	112	112
1	127	130
2	200	204
3	109	112
4	149	156
5	89	92
6	125	129
7	95	98
8	87	88
9	86	85
10	102	104
11	82	82
12	37	32
13	28	21
14	80	80
H = 4 L = 4		
0	202	206
1	21	18
2	166	172
3	71	70
4	128	130
5	143	146
6	55	55
7	60	65
8	61	65
9	132	140
10	20	25
11	61	66
12	0	4
13	83	90
H = 5 L = 4		
0	180	186
1	141	145
2	0	15
3	102	100
4	154	155
5	131	128
6	18	10
7	55	57
8	95	95
9	84	88
10	32	36
11	25	25
12	41	39
13	52	52
H = 6 L = 4		
0	0	3
1	139	140
2	60	59
3	117	120
4	102	103
5	90	94
6	77	78
7	61	66
8	89	90
9	25	29
10	68	69
11	21	16
12	69	74
H = 7 L = 4		
0	0	3
1	51	48
2	107	110
3	92	92
4	38	39
5	22	20
6	80	80
7	96	102
8	37	37
9	32	32
10	68	74
11	74	79
H = 8 L = 4		
0	62	58
1	21	19
2	135	141
3	48	47
4	44	39
5	55	56
6	70	69
7	55	57
8	25	20
9	63	60
H = 9 L = 4		
0	57	59
1	65	66
2	34	37
3	71	79
4	63	66
5	43	49
6	30	32
7	67	57
8	47	49
H =10 L = 4		
0	0	4
1	60	57
2	33	39
3	38	42
4	54	59
5	31	34
H = 0 L = 5		
1	69	73
2	157	159
3	38	42
4	108	107
5	157	156
6	58	53
7	103	100
8	180	177
9	63	63
10	75	77
11	89	91
12	86	89
13	0	1
14	27	31
H = 1 L = 5		
0	107	108
1	205	208
2	73	69
3	257	263
4	120	120
5	40	38
6	57	58
7	173	173
8	45	44
9	76	75
10	26	33
11	91	89
12	21	18
13	61	62
14	24	8
H = 2 L = 5		
0	58	55
1	199	199
2	304	315
3	69	71
4	57	58
5	112	113
6	164	165
7	32	35
8	65	61
9	72	71
10	58	58
11	48	50
12	53	55
13	25	25
14	0	12
H = 3 L = 5		
0	0	2
1	170	167
2	23	22
3	192	198
4	32	26
5	46	48
6	77	74
7	162	165
8	64	66
9	79	79
10	75	73
11	95	101
12	39	40
13	57	60

Table 4. (Continued)

K	|FO|	|FC|
H = 4 L = 5		
0	83	81
1	87	91
2	113	115
3	54	57
4	113	113
5	129	129
6	61	62
7	81	82
8	125	126
9	56	56
10	50	55
11	66	73
12	57	65
13	21	19
H = 5 L = 5		
0	152	152
1	127	131
2	108	108
3	150	156
4	127	131
5	41	39
6	43	46
7	89	91
8	58	62
9	45	40
10	42	42
11	32	36
12	23	17
H = 6 L = 5		
0	74	71
1	112	113
2	152	155
3	44	44
4	37	34
5	102	104
6	73	76
7	29	26
8	37	40
9	96	102
10	58	59
11	39	34
H = 7 L = 5		
0	55	57
1	56	53
2	50	50
3	70	71
4	79	80
5	44	37
6	69	66
7	81	82
8	75	79
9	48	51
10	68	70
H = 8 L = 5		
0	79	80
1	78	78
2	41	44
3	60	65
4	75	78
5	77	77
6	44	40
7	45	43
8	52	50
9	45	48
H = 9 L = 5		
0	101	101
1	61	53
2	70	69
3	41	43
4	80	79
5	28	23
6	39	36
7	0	20
H =10 L = 5		
0	42	38
1	44	50
2	35	34
3	0	20
H = 0 L = 6		
0	0	17
1	235	238
2	55	54
3	226	229
4	12	11
5	146	142
6	33	32
7	117	114
8	0	14
9	48	46
10	0	0
11	19	9
12	0	7
13	0	5
H = 1 L = 6		
0	180	176
1	73	73
2	29	22
3	0	10
4	144	142
5	133	132
6	99	96
7	85	87
8	112	112
9	66	64
10	120	119
11	89	91
12	34	38
13	0	3
H = 2 L = 6		
0	26	26
1	87	88
2	87	87
3	26	26
4	15	16
5	164	165
6	74	70
7	96	95
8	19	19
9	212	212
10	34	38
11	43	41
12	0	16
13	113	115
H = 3 L = 6		
0	203	210
1	144	142
2	23	19
3	102	103
4	191	192
5	115	116
6	41	41
7	0	10
8	111	113
9	41	42
10	63	65
11	38	37
12	21	18
13	0	14
H = 4 L = 6		
0	22	19
1	166	166
2	36	39
3	167	171
4	43	45
5	88	92
6	24	24
7	76	75
8	82	88
9	41	41
10	33	32
11	0	6
12	54	53
H = 5 L = 6		
0	65	61
1	21	15
2	20	12
3	85	85
4	28	30
5	69	67
6	93	96
7	111	109
8	48	53
9	46	44
10	98	101
11	86	89
H = 6 L = 6		
0	0	7
1	40	40
2	161	161
3	31	26
4	18	13
5	88	90
6	107	112
7	33	37
8	0	7
9	104	112
10	27	31
H = 7 L = 6		
0	145	142
1	116	118
2	26	16
3	97	98
4	112	114
5	55	56
6	0	8
7	35	40
8	54	54
9	26	11
H = 8 L = 6		
0	0	13
1	55	55
2	24	28
3	72	71
4	60	61
5	30	27
6	29	23
7	28	21
8	83	89
H = 9 L = 6		
0	0	21
1	40	28
2	21	14
3	76	78
4	27	26
5	0	13
H = 0 L = 7		
1	70	68
2	160	161
3	19	25
4	68	66
5	144	140
6	93	88
7	86	79
8	85	83
9	61	62
10	44	44
11	80	76
12	61	61
H = 1 L = 7		
0	39	30
1	125	125
2	90	87
3	204	202
4	52	51
5	61	60
6	20	25
7	155	156
8	30	34
9	53	51
10	22	21
11	76	80
12	0	4
H = 2 L = 7		
0	32	28
1	180	181
2	172	175
3	88	88
4	88	90
5	103	99
6	138	136
7	18	10
8	69	68
9	56	56
10	47	49
11	32	37
12	78	75
H = 3 L = 7		
0	62	61
1	113	114
2	19	19
3	158	159
4	57	57
5	51	53
6	32	31
7	140	140
8	63	61
9	61	65
10	34	28
11	80	80
12	28	28
H = 4 L = 7		
0	71	68
1	56	55
2	113	111
3	25	26
4	73	74
5	118	118
6	81	82
7	66	64
8	59	60
9	55	58
10	40	33
11	62	63
H = 5 L = 7		
0	95	100
1	77	77
2	98	98
3	130	130
4	78	82
5	29	35
6	47	49
7	90	90
8	41	41
9	31	22
10	37	39
H = 6 L = 7		
0	42	43
1	108	108
2	85	86
3	57	62
4	31	33
5	82	88
6	77	79
7	0	11
8	38	42
9	71	74
H = 7 L = 7		
0	84	75
1	48	48
2	37	37
3	68	69
4	78	83
5	38	32
6	42	45
7	67	65
8	64	68
H = 8 L = 7		
0	67	68
1	49	47
2	40	38
3	32	28
4	61	61
5	65	73
6	51	51
H = 9 L = 7		
0	68	76
1	31	28
2	55	59
3	39	43
H = 0 L = 8		
0	125	123
1	32	27
2	21	9
3	84	81
4	92	89
5	140	135
6	26	21
7	60	57
8	36	40
9	103	103
10	24	26
11	50	48
H = 1 L = 8		
0	150	150
1	141	141
2	45	44
3	56	57
4	131	130
5	129	128
6	50	53
7	24	26
8	56	55
9	75	75
10	44	46
11	48	40
H = 2 L = 8		
0	42	43
1	186	184
2	38	42
3	163	161
4	70	67
5	113	109
6	61	60
7	78	78
8	48	51
9	27	27
10	50	49
11	0	10
H = 3 L = 8		
0	74	72
1	85	85
2	87	90
3	48	48
4	90	90
5	92	90
6	81	81
7	68	65
8	42	44
9	64	65
10	66	67
11	62	65
H = 4 L = 8		
0	79	77
1	22	24
2	86	89
3	57	62
4	70	69
5	96	97
6	49	47
7	57	57
8	30	33
9	75	81
10	26	24
H = 5 L = 8		
0	127	128
1	104	105
2	37	33
3	71	71
4	107	103
5	100	98
6	0	16
7	0	31
8	40	45
9	33	44
H = 6 L = 8		
0	22	19
1	96	98
2	29	24
3	81	83
4	63	65
5	61	65
6	46	48
7	55	57
8	71	72
H = 7 L = 8		
0	19	0
1	33	29
2	69	71
3	36	44
4	37	33
5	36	33
6	64	67
7	72	72
H = 8 L = 8		
0	33	16
1	0	15
2	88	92
3	42	40
4	26	29
H = 0 L = 9		
1	122	118
2	109	107
3	132	129
4	39	32
5	119	116
6	73	70
7	41	45
8	23	20
9	30	32
10	30	28
H = 1 L = 9		
0	31	28
1	66	65
2	84	85
3	103	101
4	46	43
5	29	23
6	87	85
7	97	95
8	58	55
9	61	56
10	60	43
H = 2 L = 9		
0	37	39
1	42	40
2	44	43
3	69	68
4	60	59
5	52	50
6	71	68
7	102	101
8	84	80
9	49	46
10	50	45
H = 3 L = 9		
0	64	63
1	110	106
2	99	100
3	109	105
4	47	44
5	48	44
6	93	91
7	83	83
8	0	16
9	28	18
10	25	17
H = 4 L = 9		
0	25	16
1	95	92
2	78	80
3	88	89
4	0	19
5	91	92
6	70	72
7	27	34
8	23	20
9	24	28
H = 5 L = 9		
0	26	23
1	18	10
2	31	27
3	47	47
4	49	50
5	52	52
6	52	52
7	55	56
8	65	65
H = 6 L = 9		
0	85	83
1	74	71
2	25	25
3	60	59
4	83	80
5	50	46
6	24	28
7	56	58
H = 7 L = 9		
0	61	60
1	79	79
2	63	67
3	62	65
4	47	48
H = 0 L =10		
0	73	71
1	69	69
2	33	32
3	85	83
4	53	47
5	30	22
6	100	97
7	40	42
8	44	43
9	0	2
H = 1 L =10		
0	63	64
1	111	107
2	53	55
3	42	45
4	33	37
5	110	106
6	53	52
7	39	40
8	44	43
9	62	61
H = 2 L =10		
0	147	145
1	24	19
2	32	32
3	22	25
4	120	119
5	46	47
6	29	21
7	53	53
8	43	45
H = 3 L =10		
0	86	86
1	87	87
2	0	5
3	25	28
4	67	64
5	89	89
6	23	16
7	28	28
8	66	67
H = 4 L =10		
0	41	48
1	71	69
2	29	31
3	87	84
4	39	41
5	38	35
6	72	74
7	46	41
H = 5 L =10		
0	0	11
1	78	75
2	76	76
3	46	46
4	22	18
5	69	67
6	65	63
H = 6 L =10		
0	95	90
1	35	22
2	61	62
3	34	34
4	57	61
H = 0 L =11		
1	30	23
2	37	41
3	69	66
4	54	48
5	0	3
6	17	22
7	111	104
H = 1 L =11		
0	72	70
1	36	36
2	106	104
3	58	54
4	57	57
5	20	11
6	72	73
7	30	26
H = 2 L =11		
0	0	12
1	106	103
2	82	83
3	61	59
4	23	23
5	58	60
6	39	43
H = 3 L =11		
0	57	52
1	0	6
2	64	65
3	24	24
4	50	50
5	45	43
6	62	64
H = 4 L =11		
0	82	82
1	27	25
2	35	31
3	55	50
4	61	60
5	0	7
H = 5 L =11		
0	46	53
1	58	57
2	86	85
H = 0 L =12		
0	166	163
1	34	30
2	0	10
3	39	35
4	117	112
H = 1 L =12		
0	0	25
1	67	66
2	52	52
3	33	32
4	44	44
H = 2 L =12		
0	0	13
1	33	29
2	46	41
3	27	26
H = 3 L =12		
0	33	27
1	66	70

a weak bent hydrogen bonding to H_2O 1. The situations of water molecules H_2O 1 and H_2O 2 belong to the D- and B-types, respectively, of Chidambaram *et al.*[22] The IR spectrum showed three ν_{OH} bands at 3490, 3175 and 2880 cm^{-1}, indicating three O–H···O distances of *ca.* 2.92, 2.77 and 2.69 Å.[23] These values are in good agreement with the observed ones for the scheme mentioned above. The hydrogen atoms seem to point to one of the lone pairs of the acceptor oxygen atoms.

Magnetic Susceptibility. The magnetic susceptibility and its reciprocal are plotted against temperature in Fig. 4. Above 100 K the Curie-Weiss law holds, giving a Weiss temperature θ of $-92._6$ K and a magnetic moment $\mu_{\rm eff}$ of 2.00 β_B. At lower temperatures the susceptibility shows two maxima, one rounded and appearing at *ca.* 45 K and the other sharp and located at $26._4$ K. Below 10 K it seems to have a constant value. These features resemble those of $Cu(HCOO)_2\cdot 4H_2O$,[24,25] a blue modification of $Cu(HCOO)_2$,[26] $Cu(C_4H_4N_2)Br_2$ and other similar compounds.[27] The broad maxima were explained to be due to the one- or two-dimensional magnetic interaction and the sharp maxima to the onset of the antiferromagnetic ordering of spins throughout the crystal at the Néel temperature T_N. Constant sus-

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TABLE 5. INTERATOMIC DISTANCES (Å) AND ANGLES (°) WITH THEIR e.s.d.'s.
The subscript indicates symmetry operations given below to derive the atomic parameters.

1	x	y	z	5	$x-1/2$	$3/2-y$	$1-z$
2	$1/2-x$	$1-y$	$z+1/2$	6	$1-x$	$y-1/2$	$1/2-z$
3	$1/2-x$	$1-y$	$z-1/2$	7	$1-x$	$y-1/2$	$3/2-z$
4	$x+1/2$	$3/2-y$	$1-z$				

A. CuO_5 square pyramid			
Cu–O 1	1.946(5)	O 1–Cu–O 2	91.61(19)
Cu–O 2	1.952(4)	O 2–Cu–O 3	91.75(19)
Cu–O 3	1.963(5)	O 3–Cu–O_w 1	88.08(20)
Cu–O_w 1	1.983(5)	O_w 1–Cu–O 1	87.49(20)
Cu–O_w 2	2.325(6)	O_w 2–Cu–O 1	95.72(20)
		O_w 2–Cu–O 2	90.17(19)
O 1–O 2	2.795(6)	O_w 2–Cu–O 3	94.22(19)
O 2–O 3	2.811(6)	O_w 2–Cu–O_w 1	96.11(20)
O 3–O_w 1	2.743(7)		
O_w 1–O 1	2.717(7)	O 1–O 2–O 3	87.96(18)
O_w 2–O 1	3.177(7)	O 2–O 3–O_w 1	90.06(20)
O_w 2–O 2	3.041(7)	O 3–O_w 1–O 1	90.94(21)
O_w 2–O 3	3.152(8)	O_w 1–O 1–O 2	90.94(20)
O_w 2–O_w 1	3.213(8)		
Cu–O_w 2_7	3.116(6)	O_w 2_1–Cu–O_w 2_7	170.76(17)
B. SeO_3^{2-} anion			
Se–O 1	1.701(4)	O 1–Se–O 2	100.23(22)
Se–O 2	1.702(5)	O 2–Se–O 3	98.14(22)
Se–O 3	1.712(4)	O 3–Se–O 1	100.43(21)
O 1–O 2	2.611(6)	O 1–O 2–O 3	60.70(17)
O 2–O 3	2.580(6)	O 2–O 3–O 1	60.25(17)
O 3–O 1	2.623(6)	O 3–O 1–O 2	59.05(17)
C. Around O_w 1			
O_w 1–O 1_4	2.652(7)	O 1_4–O_w 1–O 3_5	103.39(22)
O_w 1–O 3_5	2.620(7)	O 1_4–O_w 1–O_w 2_2	89.97(21)
O_w 1–O_w 2_2	2.921(8)	O 3_5–O_w 1–O_w 2_2	83.88(21)
		Cu_1–O_w 1–O 1_4	121.83(24)
		Cu_1–O_w 1–O 3_5	123.59(24)
		Cu_1–O_w 1–O_w 2_2	124.27(24)
D. Around O_w 2			
O_w 2–O 2_2	2.729(7)	O 2_2–O_w 2–O_w 1_3	82.99(21)
O_w 2–O_w 1_3	2.921(8)	O 2_2–O_w 2–O 1_6	132.15(23)
O_w 2–O 1_6	3.364(8)	O_w 1_3–O_w 2–O 1_6	102.79(20)
		Cu_1–O_w 2–O 2_2	128.63(25)
		Cu_1–O_w 2–O_w 1_3	131.18(25)
		Cu_1–O_w 2–O 1_6	82.78(18)
		Cu_6–O_w 2–O 2_2	111.02(21)
		Cu_6–O_w 2–O_w 1_3	72.44(16)
		Cu_6–O_w 2–O 1_6	34.68(10)
		Cu_1–O_w 2–Cu_6	115.28(21)

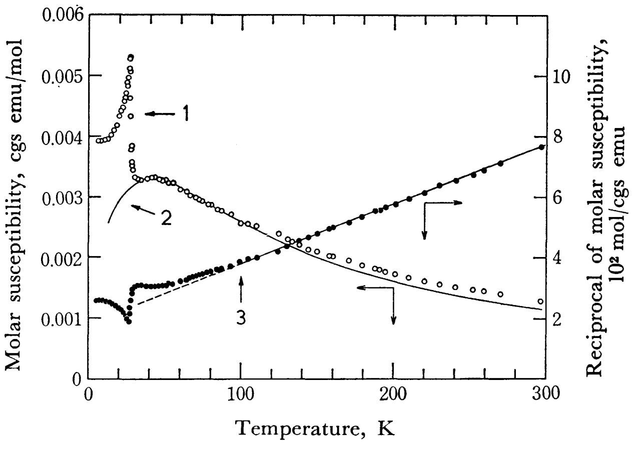

Fig. 4. Molar magnetic susceptibility and its reciprocal plotted against temperature.
1: Observed molar susceptibility, 2: calculated one for a linear Heisenberg spin system with $g=2.00$ and $J/k=-33\,K$, 3: reciprocal of the observed one.

ceptibilities below T_N were observed, and in the case of $Cu(HCOO)_2\cdot 4H_2O$[25)] the magnetization was measured to be 3% of the moment of a Cu(II) ion originating from the canting of the spins. The magnetic susceptibility of $CuSeO_3\cdot 2H_2O$ can also be explained in a similar manner.

The possible paths of superexchange interaction between magnetic ions were sought in the crystal structure. A linear path of Cu–H_2O···Cu along the crystallographic b axis is most apparent and a conformable path of magnetic interaction is known for $Cu(NH_3)_4SO_4\cdot H_2O$.[28)] However, the interaction through an H_2O molecule is very weak as is evident from the small θ and J values found in $Cu(NH_3)_4SO_4\cdot H_2O$[28)] and $CuSO_4\cdot 5H_2O$,[29)] and cannot explain the observed maximum at high temperatures. The other paths should involve SeO_3^{2-} anions. Each SeO_3^{2-} anion combines three different CuO_5 square pyramids and forms a three-dimensional network. Interatomic distances and angles concerning three Se–O–Cu paths are almost the same. If these paths contribute equally to the magnetic interaction, $CuSeO_3\cdot 2H_2O$ should be a three-dimensional ferromagnet or antiferromagnet. As a matter of fact, a broad maximum of susceptibility characteristic of the one- or two-dimensional magnet is observed. There must, therefore, be a certain difference between the three paths of Cu–O–Se–O–Cu. The environments of three oxygen atoms of an SeO_3^{2-} anion are schematically projected along the pseudosymmetry axis of the anion in Fig. 5. These oxygen atoms are also a proton acceptor. Bond angles which are made by Se, Cu and a hydrogen-donor atoms are very close to 120° except $O_w 1_4$–O 3_2–Cu_2. These values suggest that the orbitals of oxygen atoms are the sp^2 hybrid ones and that one of them is used for a σ-bond with the Se atom while the other two lone pairs are

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28) S. Saito, *J. Phys. Soc. Jap.*, **26**, 1388 (1969); and references therein.

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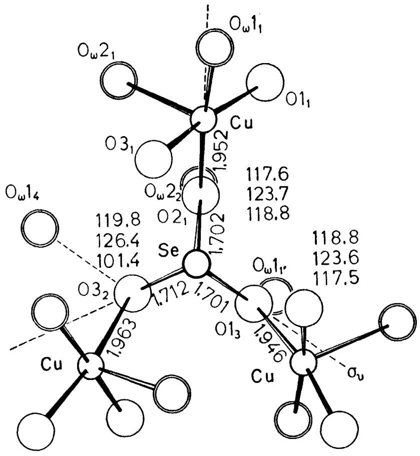

Fig. 5. Environment around an SeO_3^{2-} anion viewed along the pseudo-symmetry axis of the anion. Three numbers given for each oxygen atom of the anion are the angles of Se-O-Cu, Se-O-O(hydrogen donor) and Cu-O-O (hydrogen donor), respectively, in their order. Interatomic distances are given in Å and angles in degree.

directed towards Cu and a hydrogen-donor atoms. These sp^2 orbitals may extend within the plane normal to the basal plane of an anion and passing through the Se and O atoms, since in this conformation the oxygen atoms are bound most tightly to the Se atom by the additional formation of π-bonds. The p_π orbitals of oxygen atoms may then direct midway between the z- and x-(or y-) axes of Cu coordinate system and have only a negligible effect on the superexchange interaction between Cu atoms. The main paths of the superexchange interaction may thus involve an O–Se–O σ-bond, and the path Se–O–Cu may be weaker than the other two since the deviation of the Cu atom from the sp^2 lobus is the greatest for this oxygen atom (Fig. 5). The path Cu–O 1–Se–O 2–Cu···makes up a helical one-dimensional spin system along the crystallographic a axis. Though the difference between the three Se–O–Cu paths brings forth a linear magnetic system, the Se–O 3–Cu path may introduce a three-dimensional interaction between Cu(II) ions because the difference is not serious.

The magnetic susceptibility of $CuSeO_3 \cdot 2H_2O$ can be explained qualitatively on the refined crystal structure. Some of the parameters concerning the magnetic interactions were estimated phenomenologically. For a one-dimensional spin system there are two formalisms of magnetic susceptibility based on the Ising[30] and Heisenberg[31] spins. The Ising model could not explain the temperature dependence of the susceptibility above 30 K, while the Heisenberg model gave a fair agreement. The g and $J/\boldsymbol{k}$ values giving the best fit are 2.00 and -33 K, respectively (Fig. 4). On the other hand, the molecular field theory[32,33] gives the relationships among θ, T_N, and J values. If a single J value is assumed for three O–Se–O paths, the observed θ gives $J/\boldsymbol{k}=-31$ K, agreeing excellently with the value obtained by the Heisenberg model. The results also show that the difference in magnitude of superexchange interactions is very small. The ratio $|\theta|/T_N$ was estimated to be 3.0 using the above J value, which is comparable with the observed one (3.5). The g value of 2.00 seems smaller for a Cu(II) compound and the difference between two $J/\boldsymbol{k}$ values appears too small to give the magnetic behaviour of a linear spin system. An explanation for this may be as follows. Since each SeO_3^{2-} anion intermediates three copper(II) ions antiferromagnetically, the spin at each copper(II) cation is required to be "up" by the Cu′–O 1–Se–O 3–Cu interaction and at the same time to be "down" by the Cu″–O 2–Se–O 3–Cu interaction. The two interactions may be almost cancelled to give the observed features. The treatment is only approximate and the individual values cannot be taken to be accurate. Agreement as a whole indicates that the explanation is adequate.

In this mechanism the σ-bonds play an important role for the superexchange interaction. In $Ba_2Cu(HCOO)_6 \cdot 4H_2O$[34] and a blue modification and a royal blue one of $Cu(HCOO)_2$[26] the σ-bonds of an $HCOO^-$ anion induce a ferromagnetic spin ordering and the π-bonds an antiferromagnetic one. If these schemes for formates are applied to the present system, $CuSeO_3 \cdot 2H_2O$ should be ferromagnetic, which is contrary to observation. In the nuclear spin-spin coupling in a high resolution NMR,[35] the sign of the multibond coupling is known largely to depend on the molecular conformation even in the saturated hydrocarbons, as well as on the number of intermediate bonds. It means that the spin-spin coupling of the magnetic ion depends on the species of the intervening oxo-anions and on their conformations in the crystal structure. In fact, the very simple model without any account for the conformation leads to the antiferromagnetic coupling of two Cu(II) spins through only the σ-bonds of SeO_3^{2-} anion. Thus, it is not astonishing that $CuSeO_3 \cdot 2H_2O$ shows antiferromagnetic behaviour without any superexchange interaction through π-bonds of the anion.

The authors wish to thank Prof. Y. Shimura and Dr. S. Kaizaki, Osaka University, for their help in the measurement of diffuse reflectance spectra.

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