groups were found, in agreement with the recent review by Clearfield.[25] In the sulfate, chromate, and nitrate systems there appears to be a tendency to form linear complexes. The predominant coordination number of zirconium in these salts is eight, and the ZrO_8 polyhedra have either the symmetry of a dodecahedron ($Mo(CN)_8^{4-}$) or an antiprism.

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Structure of Manganese(II) Croconate, $C_5O_5Mn(H_2O)_3$, a One-Dimensional Coordination Polymer

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A three-dimensional single crystal X-ray examination of $C_5O_5Mn(H_2O)_3$ has established its detailed stereochemical relationship to that of the isostructural copper(II) and zinc(II) croconates which possess significant structural differences. Crystals of $C_5O_5Mn(H_2O)_3$ are orthorhombic with eight formula species in a unit cell of symmetry Pbca and of dimensions $a = 12.07$ Å., $b = 8.20$ Å., $c = 15.63$ Å. A mixed anisotropic–isotropic least-squares refinement has produced final discrepancy factors of $R_1 = 8.2\%$ and $R_2 = 10.0\%$ for the data collected photographically with Mo $K\alpha$ radiation. The polymeric structure is composed of infinite chains formed by the linkage of each manganese(II) to two adjacent oxygens of one croconate ring and to a single oxygen of another croconate ring such that only two nonadjacent oxygens per croconate are not manganese-coordinated. Each manganese(II) of similar localized environment is coordinated to six oxygens by the attachment of three waters. A comparison of the structural features of manganese(II) croconate with those of the homologous copper(II) and zinc(II) compounds is made.

Introduction

Recent X-ray studies[2] of the isostructural copper(II) and zinc(II) croconates not only have shown the overall structure of the first-row divalent transition metal croconates (which possess nearly identical powder patterns[3]) to consist of polymeric chains but also have revealed important differences in their detailed stereochemistry. In addition to a marked distortion of the oxygen environment for the six-coordinated d^9 copper(II) as contrasted to the more regular environment of the d^{10} zinc(II), the geometries of the croconate rings in the two metal complexes are different. The D_{5h} symmetry of the "free" electron-delocalized croconate dianion,[4] $C_5O_5^{2-}$, is essentially retained in copper(II) croconate, whereas in zinc(II) croconate the croconate ring of *idealized* C_{2v} symmetry is related to that of the localized α-enediol, croconic acid. In order to obtain further experimental evidence concerning the extent of the Jahn–Teller effect in determining the stereochemistry of this homologous series of oxygen-coordinated divalent metal ions, a three-dimensional X-ray investigation of the high-spin d^5 manganese(II) croconate (which like the zinc(II) electronic configuration does not exhibit Jahn–Teller instability) was carried out. The preparation and characterization of these transition metal complexes of general formula $C_5O_5M(H_2O)_3$ (where M = Mn, Fe, Co, Ni, Cu, and Zn) are given by West and Niu.[3]

Experimental Section

Crystals of $C_5O_5Mn(H_2O)_3$ were generously made available by Professor R. C. West and Dr. H. Y. Niu of the University of Wisconsin. Lattice parameters were obtained from *hk*0 and 0*kl* photographs with a NaCl-calibrated precession camera. Multiple-film equi-inclination Weissenberg photographs were obtained with Zr-filtered Mo $K\alpha$ radiation for nine reciprocal levels, *h*0*l* through *h*8*l*. A total of 807 observed, independent maxima were measured by visual estimation with a calibrated set of intensities and then corrected for Lorentz-polarization effects. The crystal utilized for collecting the Weissenberg intensity data was sufficiently small ($\mu R_{max} < 0.5$) that absorption corrections were not made.

Results

Unit Cell and Space Group.—Crystals of $C_5O_5Mn(H_2O)_3$ are orthorhombic with lattice parameters a =

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[3] R. West and H. Y. Niu, *J. Am. Chem. Soc.*, **85**, 2586 (1963).

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12.07 ± 0.03 Å., $b = 8.20 \pm 0.02$ Å., $c = 15.63 \pm 0.04$ Å. The axial ratios for these cell parameters are given below along with those calculated from the X-ray data previously reported[2] for the isostructural copper(II) and zinc(II) croconates.

$C_5O_5Mn(H_2O)_3,\ a:b:c = 1.472:1:1.906$

$C_5O_5Cu(H_2O)_3,\ a:b:c = 1.455:1:1.923$

$C_5O_5Zn(H_2O)_3,\ a:b:c = 1.469:1:1.882$

The space group Pbca, uniquely defined by the systematic extinctions of $k = 2n + 1$ for $\{0kl\}$, $l = 2n + 1$ for $\{h0l\}$, and $h = 2n + 1$ for $\{hk0\}$, was verified by the satisfactory refinement of the structure. For eight formula species of $C_5O_5Mn(H_2O)_3$ per unit cell, this centrosymmetric space group requires (with no atoms located on centers of symmetry) the determination of the parameters of fourteen independent nonhydrogen atoms comprised of one manganese, five carbons, and eight oxygens, each of which occupies the general eightfold set of positions (8c): $\pm(x, y, z;\ {}^1/_2 + x, {}^1/_2 - y, \bar{z};\ \bar{x}, {}^1/_2 + y, {}^1/_2 - z;\ {}^1/_2 - x, \bar{y}, {}^1/_2 + z)$.[5]

Determination of the Structure.—The structure was solved from a combination of Patterson and Fourier syntheses. An isotropic least-squares refinement with individual thermal parameters and a separate scale factor per Weissenberg reciprocal layer converged rapidly to give discrepancy factors of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100 = 9.8\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100 = 11.5\%$. Further refinement with anisotropic thermal parameters for the manganese(II) and individual isotropic thermal parameters for the other atoms yielded final discrepancy factors of $R_1 = 8.2\%$ and $R_2 = 10.0\%$. During the last cycle no coordinate changed by more than 0.6 of its standard deviation. The final parameters were in close agreement with the corresponding ones for the isotropic least-squares refinement. Of the 42 positional parameters, 38 differed by less than 1σ, and the remaining 4 by less than 2σ. Of the 13 atomic isotropic thermal parameters utilized for the light atoms in the mixed anisotropic–isotropic refinement, 6 differed by less than 1σ, 6 by 1–2σ, and 1 by 2–3σ. For photographic data it is well known that the thermal parameters are unusually sensitive to systematic errors, and the use of variable interlayer scale factors for the Weissenberg data *consequently* does not allow any physical interpretation of the thermal parameters in terms of r.m.s. atomic displacements. However, the invariance of the positional parameters to both thermal models and the very low positional–thermal interaction constants obtained from the correlation matrices indicate that the reported estimated standard deviations of the bond lengths and angles calculated from a full inverse matrix are reasonably realistic. It is felt that the calculated isotropic–anisotropic thermal model provides more meaningful positional parameters (where small differences do exist), since any anisotropic thermal model (even with large interactions of the scale factors and thermal parameters as seen from the correlation matrices) should conform more nearly to the physical situation.

TABLE I

FINAL ATOMIC PARAMETERS WITH STANDARD DEVIATIONS FROM ANISOTROPIC–ISOTROPIC LEAST-SQUARES REFINEMENT

	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10^2\sigma_B$)
Mn	0.1237 (2)	0.1161 (2)	0.1860 (1)	[a]
C(1)	0.1220 (11)	0.0704 (12)	0.3689 (7)	1.54 (18)
C(2)	0.1328 (10)	0.2443 (14)	0.3579 (7)	1.75 (18)
C(3)	0.1335 (10)	0.3226 (12)	0.4407 (7)	1.41 (18)
C(4)	0.1312 (11)	0.1890 (11)	0.5037 (7)	1.34 (17)
C(5)	0.1247 (10)	0.0291 (10)	0.4612 (6)	1.00 (16)
O(1)	0.1156 (7)	−0.0289 (9)	0.3083 (5)	2.02 (15)
O(2)	0.1328 (8)	0.3040 (9)	0.2837 (5)	2.18 (15)
O(3)	0.1317 (7)	0.4691 (8)	0.4551 (5)	1.57 (14)
O(4)	0.1380 (7)	0.2046 (8)	0.5843 (5)	1.85 (16)
O(5)	0.1194 (8)	−0.0994 (9)	0.4949 (5)	2.43 (15)
O(6)	0.1092 (7)	−0.1001 (8)	0.1141 (5)	1.91 (14)
O(7)	−0.0571 (7)	0.1545 (8)	0.1761 (6)	1.90 (15)
O(8)	0.3074 (7)	0.0979 (9)	0.1773 (6)	2.21 (15)

[a] For the manganese atom the anisotropic temperature factors are of the form $\exp\{-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})\}$; the resulting thermal coefficients ($\times 10^4$) with e.s.d. in parentheses are: $B_{11} = 32$ (1); $B_{22} = 54$ (5); $B_{33} = 8$ (1); $B_{12} = 2$ (2); $B_{13} = 1$ (1); $B_{23} = -1$ (1).

The electron density and Patterson functions were computed with the Blount Fourier program.[6] The refinement and error analyses were carried out with local versions of the Busing–Martin–Levy programs.[7] The full-matrix least-squares refinements were based on the observed structure factors with variable weighting given by the function $\sqrt{w} = (2/F_o)(I_o/I_{\min})^2$ if $I_o < \sqrt{10}I_{\min}$ and $\sqrt{w} = 20/F_o$ if $I_0 \geq \sqrt{10}I_{\min}$. Scattering factors given by Watson and Freeman[8] were used for manganese(II), while those of Hanson, *et al.*,[9] were chosen for oxygen and carbon.

Table I lists the final positional and thermal parameters with their standard deviations obtained from the mixed anisotropic–isotropic least-squares refinement. A comparison of the observed and calculated structure factors based on these atomic parameters is given in Table II. The intrachain bond lengths and angles with their standard deviations are given in Tables III and IV; the estimated standard deviations obtained from the full inverse matrix include the uncertainties in unit cell parameters.

Discussion

The structure of $C_5O_5Mn(H_2O)_3$ consists of infinite chains with each manganese(II) of identical localized environment coordinated to two adjacent oxygens of one croconate ring and to a single oxygen of a second croconate ring such that only two nonadjacent oxygens per croconate ring are not metal-coordinated. The

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(5) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 150. The two misprints of the positional parameters given in ref. 2 have been corrected.

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(8) A. J. Freeman and R. E. Watson, *Acta Cryst.*, **14**, 231 (1961).

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TABLE II

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	FO	FC
0	0	6	209	220
0	0	8	188	-178
0	0	10	136	112
0	0	14	63	-71
0	0	16	99	102
0	0	22	70	69
1	0	4	115	112
1	0	6	41	34
1	0	8	49	46
1	0	10	114	113
1	0	12	112	-105
1	0	18	52	-50
3	0	2	41	33
3	0	6	62	57
3	0	8	70	66
3	0	10	57	49
3	0	12	68	-70
3	0	18	33	-33
4	0	4	20	-22
4	0	6	87	-109
4	0	8	104	100
4	0	10	90	-88
4	0	12	31	27
4	0	14	28	35
4	0	6	107	-109
4	0	22	57	-56
5	0	2	58	43
5	0	4	109	-111
5	0	8	26	-25
5	0	10	112	-114
5	0	12	95	96
5	0	18	47	49
6	0	2	21	18
6	0	6	26	-22
7	0	2	27	24
7	0	4	58	-55
7	0	8	33	-26
7	0	10	55	-51
7	0	12	63	60
7	0	18	33	33
8	0	0	212	259
8	0	4	24	26
8	0	6	48	45
8	0	8	48	-47
8	0	10	55	52
8	0	12	34	-33
8	0	16	53	56
8	0	18	29	-26
8	0	22	43	42
9	0	4	43	35
9	0	8	32	31
9	0	10	51	54
9	0	12	54	-53
9	0	18	31	-27
11	0	2	37	-33
11	0	4	63	60
11	0	10	52	46
11	0	12	50	-45
12	0	0	133	-161
12	0	6	59	-58
12	0	8	52	51
12	0	10	35	-28
12	0	16	46	-44
13	0	10	33	-33
13	0	12	37	34
16	0	0	73	87
16	0	6	38	39
16	0	8	36	-33
1	1	4	82	83
1	1	7	66	-57
1	1	6	60	-57
1	1	9	51	-48
1	1	10	90	94
1	1	12	79	-79
1	1	13	53	-51
1	1	17	28	27
1	1	18	34	-33
1	1	20	30	30
2	1	2	31	34
2	1	3	29	30
2	1	4	16	-9
2	1	5	99	106
2	1	7	54	-51
2	1	8	84	87
2	1	9	59	56
2	1	10	26	-23
2	1	11	70	-76
2	1	13	33	-29
2	1	14	21	-12
2	1	15	61	60
2	1	16	27	-31
2	1	17	58	-60
2	1	18	30	30
2	1	19	24	16
2	1	21	26	19
2	1	22	34	-35
3	1	1	19	17
3	1	2	39	-28
3	1	3	25	27
3	1	5	10	4
3	1	6	20	18
3	1	7	65	61
3	1	8	24	-22
3	1	9	31	24
3	1	10	60	-54
3	1	12	60	62
3	1	13	43	42
3	1	18	25	21
3	1	20	29	-27
4	1	0	65	64
4	1	1	49	-42
4	1	7	17	-11
5	1	1	23	-19
5	1	2	30	27
5	1	3	104	104
5	1	4	83	-82
5	1	5	25	-20
5	1	6	59	57
5	1	7	42	40
5	1	9	49	46
5	1	10	75	-75
5	1	11	39	-37
5	1	12	61	64
5	1	13	45	46
5	1	17	29	-30
5	1	18	32	30
5	1	20	25	-26
6	1	0	187	219
6	1	1	142	157
6	1	2	70	-72
6	1	3	37	-38
6	1	5	105	-108
6	1	6	60	58
6	1	7	91	93
6	1	8	96	-102
6	1	9	69	-65
6	1	10	28	23
6	1	11	45	45
6	1	13	45	46
6	1	15	60	-64
6	1	16	32	37
6	1	17	47	50
6	1	21	31	-27
6	1	22	34	37
6	1	23	27	23
7	1	3	45	-45
7	1	5	38	35
7	1	7	48	-43
7	1	9	40	-37
7	1	10	47	46
7	1	12	54	-56
7	1	13	35	-34
7	1	18	27	-21
8	1	0	43	-50
8	1	1	32	33
8	1	2	17	-16
9	1	3	37	-37
9	1	4	33	30
9	1	6	34	-31
9	1	7	23	-26
9	1	10	28	27
9	1	12	33	-31
9	1	13	25	-26
10	1	0	101	-109
10	1	1	74	-77
10	1	2	33	35
10	1	5	48	51
10	1	6	35	-32
10	1	7	50	-53
10	1	8	51	52
10	1	9	36	36
10	1	11	26	-29
10	1	13	24	-26
10	1	15	39	40
10	1	16	26	-27
10	1	17	35	-35
11	1	3	36	38
11	1	4	29	-26
11	1	5	34	-37
11	1	7	28	27
11	1	9	34	34
11	1	10	37	-39
11	1	11	22	-18
11	1	12	45	46
11	1	13	24	23
12	1	0	30	34
13	1	3	20	20
13	1	4	24	-24
13	1	6	21	20
13	1	12	23	19
14	1	0	37	43
14	1	1	23	26
14	1	11	24	19
14	1	17	27	22
15	1	10	22	16
15	1	12	27	-26
0	2	4	27	22
0	2	5	154	173
0	2	6	58	58
0	2	7	181	-190
0	2	8	42	-38
0	2	9	96	98
0	2	12	49	-50
0	2	13	68	-67
0	2	14	66	-64
0	2	15	90	89
0	2	17	61	-57
0	2	21	53	51
1	2	3	90	96
1	2	4	88	86
1	2	5	183	-189
1	2	7	64	58
1	2	9	65	64
1	2	11	77	-71
1	2	13	51	48
1	2	17	33	-30
1	2	19	27	29
1	2	21	31	-29
2	2	2	14	12
2	2	6	24	-19
3	2	2	21	19
3	2	4	46	46
3	2	5	135	-133
3	2	6	35	36
3	2	7	54	56
3	2	9	31	27
3	2	11	51	-46
3	2	13	33	32
3	2	15	31	-28
3	2	21	31	-33
4	2	0	34	-33
4	2	1	53	53
4	2	2	14	-15
4	2	3	81	-84
4	2	4	17	-16
4	2	5	91	-93
4	2	6	44	-47
4	2	7	98	101
4	2	8	37	33
4	2	9	56	-61
4	2	12	44	42
4	2	13	37	32
4	2	14	60	57
4	2	15	62	-62
4	2	17	53	52
4	2	21	38	-37
5	2	1	49	52
5	2	2	28	-29
5	2	3	101	-102
5	2	4	54	-54
5	2	5	143	141
5	2	6	25	-25
5	2	7	47	-45
5	2	9	59	-59
5	2	11	60	59
5	2	12	26	-22
5	2	13	49	-47
5	2	17	34	34
6	2	0	29	-33
7	2	1	23	24
7	2	2	25	-23
7	2	3	39	-39
7	2	5	106	110
7	2	6	28	-29
7	2	7	35	-35
7	2	9	38	-37
7	2	11	57	58
7	2	13	24	-26
7	2	21	29	27
7	2	8	20	-21
8	2	0	19	23
8	2	1	22	-18
8	2	3	40	40
8	2	5	39	39
8	2	7	43	-40
8	2	8	25	-23
8	2	9	31	33
8	2	12	30	-30
8	2	14	43	-42
8	2	15	39	39
8	2	17	40	-40
9	2	1	19	-16
9	2	3	34	32
9	2	4	37	37
9	2	5	47	-50
9	2	7	36	33
9	2	13	27	33
10	2	0	41	48
10	2	8	20	-7
11	2	1	25	-24
11	2	3	44	46
11	2	5	63	-76
11	2	9	34	35
11	2	11	51	-55
12	2	1	46	46
12	2	3	24	-24
12	2	5	39	-41
12	2	7	46	47
12	2	9	33	-32
12	2	15	35	-38
13	2	3	23	-20
13	2	4	24	-29
13	2	7	22	-22
14	2	0	24	-29
15	2	5	30	33
15	2	11	28	30
16	2	1	33	-33
16	2	5	25	26
1	3	3	136	153
1	3	4	113	141
1	3	5	84	-91
1	3	6	73	-79
1	3	7	51	47
1	3	9	37	39
1	3	10	53	53
1	3	11	33	-30
1	3	12	40	-40
1	3	13	60	55
1	3	14	22	18
2	3	2	53	62
2	3	5	45	-45
2	3	6	42	-37
2	3	7	28	25
2	3	8	96	104
2	3	10	21	16
2	3	12	35	32
2	3	13	22	20
2	3	14	63	64
2	3	15	45	-44
2	3	16	37	-38
2	3	18	36	36
3	3	1	12	-11
3	3	3	71	-79
3	3	4	90	-102
3	3	5	45	50
3	3	6	48	49
3	3	7	51	-47
3	3	10	28	-24
3	3	12	27	27
3	3	13	49	-44
3	3	14	26	-21
3	3	15	21	12
3	3	22	30	25
4	3	0	26	-23
4	3	1	18	-14
4	3	2	26	22
4	3	5	19	20
4	3	7	28	-27
4	3	8	27	22
5	3	1	29	28
5	3	2	43	41
5	3	3	96	-105
5	3	4	121	-135
5	3	5	59	61
5	3	6	73	82
5	3	7	41	-38
5	3	8	21	16
5	3	9	32	-28
5	3	10	67	-70
5	3	11	26	26
5	3	12	48	48
5	3	13	55	-49
5	3	18	28	30
5	3	19	25	-24
5	3	20	27	-25
6	3	0	41	40
6	3	1	36	-31
6	3	2	74	-75
6	3	3	26	22
6	3	5	58	61
6	3	6	61	65
6	3	7	58	-58
6	3	8	96	-106
6	3	9	22	22
6	3	13	39	-37
6	3	14	68	-70
6	3	15	49	48
6	3	16	44	39
6	3	18	29	-27
6	3	20	25	-17
6	3	22	31	30
7	3	2	33	-33
7	3	3	51	50
7	3	4	88	95
7	3	5	35	-36
7	3	6	36	-34
7	3	7	36	34
7	3	10	36	29
7	3	12	30	-29
7	3	13	34	32
9	3	3	36	39
9	3	4	60	63
9	3	5	23	-20
9	3	6	43	-48
9	3	10	44	42
9	3	12	28	-30
9	3	13	33	33
9	3	7	27	26
10	3	0	37	-32
10	3	1	21	17
10	3	2	42	40
10	3	3	22	-15
10	3	5	34	-33
10	3	6	37	-34
10	3	7	34	30
10	3	8	57	61
10	3	12	22	12
10	3	13	25	22
10	3	14	48	47
10	3	15	30	-30
10	3	16	30	-27
11	3	2	33	28
11	3	3	44	-44
11	3	4	54	-59
11	3	5	32	32
11	3	7	27	-20
11	3	9	23	-21
11	3	10	26	-20
11	3	12	27	21
11	3	13	30	-23
13	3	3	24	-27
13	3	4	28	-28
13	3	6	24	26
13	3	10	25	-24
0	4	4	19	23
0	4	5	30	-26
0	4	6	111	-121
0	4	8	71	70
0	4	9	28	27
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0	4	14	64	64
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1	4	9	30	23
1	4	10	43	-36
1	4	11	71	-70
1	4	12	64	61
1	4	14	49	-46
1	4	16	26	-19
1	4	20	42	-39
3	4	1	21	-26
3	4	2	69	83
3	4	4	57	-60
3	4	5	52	-55
3	4	6	50	49
3	4	11	56	-57
3	4	12	51	50
3	4	14	52	-48
3	4	20	39	-36
4	4	0	59	64
4	4	1	50	50
4	4	2	53	-57
4	4	6	67	68
4	4	8	39	-37
4	4	9	22	-22
4	4	10	74	77
4	4	12	29	25
4	4	14	48	-40
4	4	16	68	67
5	4	1	23	25
5	4	2	82	-93
5	4	3	28	32
5	4	4	81	93
5	4	6	59	-62
5	4	8	36	-32
5	4	10	40	35
5	4	11	46	43
5	4	12	51	-49
5	4	14	40	36
5	4	20	36	35
7	4	2	74	-76
7	4	3	22	24
7	4	4	62	61
7	4	5	32	31
7	4	6	41	-42
7	4	10	28	26
7	4	11	32	29
7	4	12	50	-49
7	4	14	42	36
7	4	20	37	31
8	4	0	30	-24
8	4	1	36	-34
8	4	2	35	30
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8	4	10	54	-54
8	4	16	50	-49
9	4	2	37	34
9	4	4	37	-36
9	4	6	34	35
9	4	11	32	-29
9	4	14	29	-26
10	4	0	26	-24
11	4	2	52	56
11	4	4	53	-49
11	4	5	32	-29
11	4	6	30	33
11	4	10	30	-29
11	4	11	23	-24
11	4	12	41	41
12	4	0	40	34
12	4	2	37	-34
12	4	6	35	35
12	4	8	36	-30
12	4	10	37	36
12	4	16	37	37
1	5	3	56	70
1	5	4	31	-36
1	5	5	19	-16
1	5	6	23	18
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1	5	11	60	-63
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1	5	20	34	-24
1	5	21	32	-24
1	5	9	21	12
2	5	2	47	-58
2	5	3	26	26
2	5	4	24	24
2	5	6	26	24
2	5	7	39	33
2	5	8	56	-52
2	5	9	61	-59
2	5	10	64	62
2	5	11	36	32
2	5	12	24	23
2	5	15	33	-34
2	5	16	41	38
2	5	17	34	36
2	5	23	32	31
2	5	24	31	-24
3	5	1	20	23
4	5	5	26	-28
4	5	1	16	20
4	5	0	16	-17
3	5	2	30	-34
3	5	3	44	-47
3	5	8	32	-28
3	5	11	57	60
3	5	13	36	-32
3	5	19	35	-30
3	5	20	27	24
3	5	21	30	24
5	5	8	30	-25
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6	5	6	40	-39
6	5	7	50	-49
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7	5	13	25	22
7	5	19	37	29
7	5	20	26	-21
7	5	21	28	-20
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9	5	3	54	54
9	5	5	30	-28
9	5	11	40	-37
9	5	13	45	40
9	5	19	30	21
10	5	1	60	65
10	5	2	34	-34
10	5	7	39	33
10	5	8	42	-35
10	5	9	41	-37
10	5	10	39	35
10	5	15	32	-25
10	5	16	30	26
11	5	1	19	14
11	5	2	30	-28
11	5	3	27	-22
11	5	5	28	23
11	5	11	46	43
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14	5	1	29	-30
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0	6	5	16	-11
0	6	6	35	-34
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0	6	8	35	-30
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0	6	17	43	38
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1	6	6	52	49
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1	6	9	29	-18
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3	6	4	19	-18
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4	6	7	81	-78
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5	6	1	37	-37
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5	6	5	35	-33
5	6	6	40	-38
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7	6	3	23	17
7	6	5	37	-37
7	6	11	32	-34
8	6	0	21	-17
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8	6	2	22	21
8	6	3	25	-22
8	6	4	28	28
8	6	6	30	-24
8	6	7	50	48
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9	6	5	23	15
9	6	6	29	30
9	6	11	39	39
10	6	0	30	-32
11	6	5	36	33
11	6	11	31	23
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12	6	7	39	-37
12	6	9	44	43
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1	7	3	20	-26
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1	7	5	17	16
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1	7	9	23	-17
6	7	18	47	39
6	7	16	34	-33
1	7	10	20	-16
1	7	11	29	28
1	7	14	25	-23
2	7	3	18	18
2	7	4	30	-35
2	7	5	14	-13
2	7	6	47	56
2	7	7	27	-25
2	7	8	66	-65
2	7	9	43	44
2	7	10	32	33
2	7	14	41	-31
2	7	16	42	36
2	7	18	56	-47
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3	7	2	22	-22
3	7	6	56	-63
3	7	10	18	15
3	7	11	21	-20
3	7	12	20	-18
3	7	14	28	26
4	7	0	21	26
4	7	1	18	20
4	7	8	28	-25
5	7	1	16	-16
5	7	2	26	-28
5	7	4	31	29
5	7	6	54	-58
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5	7	10	32	29
5	7	12	24	-23
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6	7	2	90	92
6	7	4	30	31
6	7	6	51	-50
6	7	7	31	29
6	7	8	57	56
6	7	9	40	-38
6	7	10	30	-30
6	7	13	24	20
6	7	14	36	30
7	7	1	19	19
7	7	2	36	35
7	7	4	27	-22
7	7	10	23	-21
7	7	11	24	12
7	7	12	26	22
7	7	14	26	-24
7	7	16	26	-22
9	7	2	20	19
9	7	4	26	-21
9	7	6	36	38
10	7	2	57	-62
10	7	4	24	-24
10	7	6	36	32
10	7	7	24	-19
10	7	8	39	-36
10	7	9	28	25
10	7	10	28	23
10	7	16	28	25
10	7	18	29	-28
11	7	2	22	-24
11	7	6	35	-37
0	8	3	19	-21
0	8	4	19	-15
0	8	5	18	-14
0	8	6	55	53
0	8	7	48	44
0	8	8	52	-48
0	8	9	28	-23
0	8	10	25	20
0	8	14	52	-47
0	8	15	36	-27
0	8	16	41	28
1	8	4	40	43
1	8	5	42	44
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1	8	10	25	19
1	8	11	29	22
1	8	12	31	-23
1	8	14	36	27
3	8	2	28	-32
3	8	4	35	37
3	8	5	35	36
3	8	6	29	-24
3	8	12	28	-22
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4	8	8	46	42
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5	8	1	23	12
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5	8	4	43	-37
5	8	5	26	-22
5	8	6	33	30
5	8	14	37	-24
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7	8	4	33	-30
8	8	0	25	18
8	8	1	27	21
8	8	2	32	-32
8	8	6	38	32
8	8	7	38	27
8	8	8	39	-33
8	8	14	38	-32
9	8	2	27	-15
9	8	4	32	24
9	8	6	33	-23
11	8	2	30	-23
11	8	4	31	22
12	8	2	32	23
12	8	6	33	-22
12	8	8	37	26

TABLE III

BOND LENGTHS (Å.) WITH STANDARD DEVIATIONS[a]

Mn–O(1)	2.253 ± 0.008
Mn–O(2)	2.172 ± 0.008
Mn–O(4^{I})	2.172 ± 0.007
Mn–H_2O(6)	2.106 ± 0.007
Mn–H_2O(7)	2.210 ± 0.008
Mn–H_2O(8)	2.226 ± 0.009
C(1)–C(2)	1.442 ± 0.015
C(2)–C(3)	1.445 ± 0.014
C(3)–C(4)	1.473 ± 0.014
C(4)–C(5)	1.472 ± 0.013
C(5)–C(1)	1.482 ± 0.014
C(1)–O(1)	1.252 ± 0.013
C(2)–O(2)	1.259 ± 0.013
C(3)–O(3)	1.222 ± 0.013
C(4)–O(4)	1.269 ± 0.012
C(5)–O(5)	1.180 ± 0.012

[a] Superscript I refers to the position (x, $^1/_2 - y$, $-^1/_2 + z$).

asymmetric repeating unit comprised of one manganese(II), one croconate ring, and three waters is shown in Figure 1. The chains are parallel to the *c* axis with the crystallographic identity period containing two $C_5O_5Mn(H_2O)_3$ units. The six-coordinated manganese(II) is surrounded by three croconate oxygens and three waters at the corners of a distorted octahedron.

Since a discussion of the detailed structural characteristics of the isostructural copper(II) and zinc(II) complexes already has been presented, the prime purpose of this discussion is to compare the geometric features of the manganese coordination sphere and of the croconate ring with those in the copper(II) and zinc(II) croconates.

Examination of the bond lengths and angles shows the oxygen environment about the manganese(II) to parallel closely that about the zinc(II). The average Mn–O distance of 2.19 Å. for the six bonds is 0.08 Å. longer than the average Zn–O distance of 2.11 Å. This

Table IV

Bond Angles (degrees) with Standard Deviations[a]

O(1)–Mn–O(2)	77.3 ± 0.3
O(1)–Mn–H_2O(6)	90.3 ± 0.3
O(1)–Mn–H_2O(7)	95.3 ± 0.3
O(1)–Mn–H_2O(8)	93.4 ± 0.3
O(2)–Mn–H_2O(7)	89.9 ± 0.3
O(2)–Mn–H_2O(8)	92.3 ± 0.3
O(2)–Mn–O(4^I)	91.7 ± 0.3
H_2O(6)–Mn–H_2O(7)	90.0 ± 0.3
H_2O(6)–Mn–H_2O(8)	89.6 ± 0.3
H_2O(6)–Mn–O(4^I)	100.7 ± 0.3
H_2O(7)–Mn–O(4^I)	86.0 ± 0.3
H_2O(8)–Mn–O(4^I)	85.5 ± p.3
O(1)–Mn–O(4^I)	168.9 ± 0.3
O(2)–Mn–H_2O(6)	167.5 ± 0.3
H_2O(7)–Mn–H_2O(8)	171.3 ± 0.3
Mn–O(1)–C(1)	107.2 ± 0.6
Mn–O(2)–C(2)	111.8 ± 0.7
Mn–O(4^I)–C(4^I)	142.2 ± 0.6
C(1)–C(2)–C(3)	109.5 ± 0.9
C(2)–C(3)–C(4)	105.6 ± 0.8
C(3)–C(4)–C(5)	111.2 ± 0.8
C(4)–C(5)–C(1)	103.7 ± 0.7
C(5)–C(1)–C(2)	109.9 ± 0.9
O(2)–C(2)–C(3)	130.7 ± 1.0
C(2)–C(3)–O(3)	127.0 ± 0.9
O(3)–C(3)–C(4)	127.4 ± 0.9
C(3)–C(4)–O(4)	126.0 ± 0.8
O(4)–C(4)–C(5)	122.8 ± 0.8
C(4)–C(5)–O(5)	126.7 ± 0.9
O(5)–C(5)–C(1)	129.6 ± 0.9
C(5)–C(1)–O(1)	126.1 ± 0.9
O(1)–C(1)–C(2)	124.0 ± 1.0
C(1)–C(2)–O(2)	119.6 ± 1.0

[a] Superscript I refers to the position (x, $^1/_2 - y$, $-^1/_2 + z$).

difference is consistent with the difference of 0.08 Å. given[10] for the ionic (and also the covalent) radii of the two metals. A similar *average* metal–fluorine difference of 0.08 Å. was observed for the homologous difluoride compounds, MnF_2 and ZnF_2, which possess the rutile structure.[11] All O–Mn–O angles are within 2° of the corresponding O–Zn–O angles. These similarities show that in the replacement of the d^{10} zinc(II) by the d^5 manganese(II) the same localized stereochemical oxygen environment essentially has been retained except for the expected change in bond lengths. Consequently, the significant departures of the oxygen atoms about the d^9 copper(II) from this environment[2] are attributable primarily to the static Jahn–Teller effect.

The reduced C_{2v} symmetry indicated for the croconate ring in zinc(II) croconate (as opposed to the *idealized* D_{5h} symmetry found for the croconate ring in copper(II) croconate) suggests a partial localization of the π electrons. This proposed *quasi*-croconic acid structure for zinc(II) croconate is based on the following three geometric features: (1) the short C(1)–C(2) ring bond (1.42 Å.) compared to the other four croconate ring bonds (1.49 Å. (av)), (2) the "normal" ketonic C–O bond lengths of the two uncoordinated oxygens (1.20 Å. (av)) compared to the other three zinc-coordinated C–O bond lengths (1.25 Å. (av)), and (3) the ring angles subtended at the essentially ketonic carbons, C(3) and C(5), possessing significantly smaller angles (103° (av)) than the other three inner ring angles (111° (av)). Of these three corresponding features in manganese(II) croconate, only the first one is not in apparent agreement. Although the C(1)–C(2) bond length of 1.44 Å. is one of the two shortest ring bonds, it is not significantly shorter than the other four bonds (1.47 Å. (av)). However, both the shorter uncoordinated C–O bonds (1.20 Å. (av) *vs.* 1.26 Å. (av) for the three metal-coordinated bonds) and the two smaller inner ring angles subtended at the ketonic carbons (105° (av) *vs.* 110° (av) for the other three angles) distinctly do conform to the lower *idealized* symmetry characteristic of a trend toward an enediol configuration.

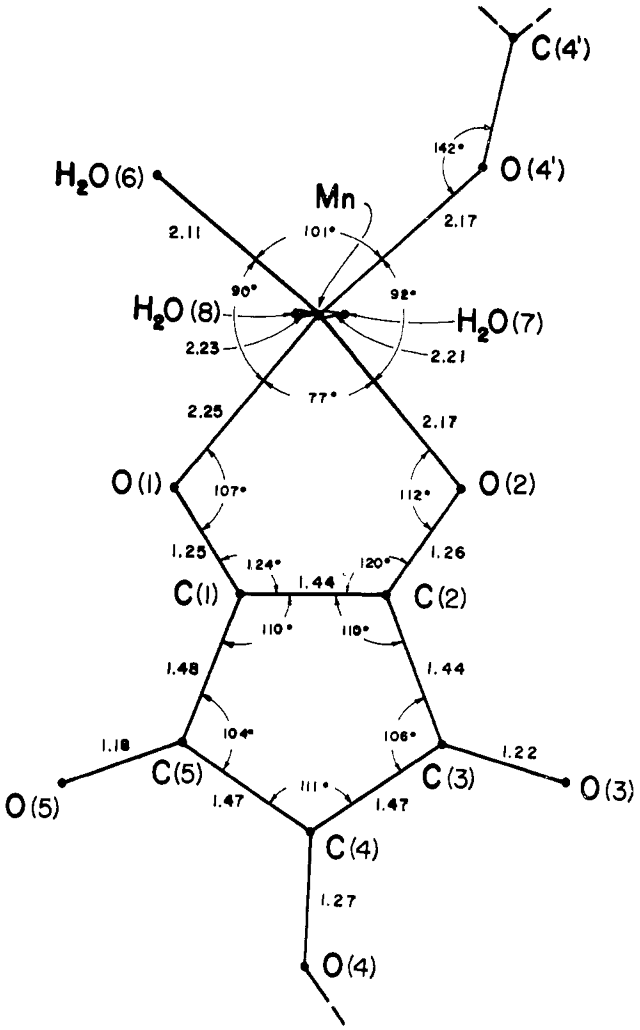

Figure 1.—The configuration of the asymmetric repeating unit of $C_5O_5Mn(H_2O)_3$ with bond lengths and angles.

The indicated similarities in the croconate ring dimensions for the manganese(II) and zinc(II) croconates as contrasted to those in copper(II) croconate therefore may be a manifestation of the different stereochemical requirements imposed by the central metals in forming these oxygen-coordinated polymers.

In similar fashion to that present in both copper(II) and zinc(II) croconates, the five croconate ring carbons are essentially coplanar with two croconate oxygens,

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[10] *Cf.* T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952.

[11] R. D. Peacock, *Progr. Inorg. Chem.*, **2**, 193 (1960).

O(3) and O(4), distorted out of the *mean* croconate carbon plane. The hydrogen-bonding network presumably responsible for this and other small but significant chain deformations is analogous to those previously discussed in detail for the $C_5O_5Cu(H_2O)_3$ and $C_5O_5Zn(H_2O)_3$ compounds. The magnitudes of the closest intra- and interchain nonbonding distances in manganese(II) croconate closely parallel those in zinc(II) croconate.[12]

[12] The transformations in Table V of ref. 2 should be corrected as follows. IV: $-\frac{1}{2} + x, y, \frac{1}{2} - z$. VI: $x, \frac{1}{2} - y, -\frac{1}{2} + z$.

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CONTRIBUTION FROM THE MELLON INSTITUTE,
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Organonitrogen Derivatives of Metal Carbonyls. I. Reactions between Metal Carbonyl Anions and Haloalkyl Amines[1]

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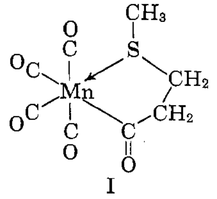
2-Chloroethyldimethylamine reacts with $NaMn(CO)_5$ to give the yellow crystalline cyclic acyl derivative $(CH_3)_2NCH_2CH_2COMn(CO)_4$. Similarly, 2-chloroethyldimethylamine reacts with $NaFe(CO)_2C_5H_5$ to give the dark red crystalline cyclic acyl derivative $(CH_3)_2NCH_2CH_2COFeCOC_5H_5$ and the yellow-orange salt $[(CH_3)_2NCH_2CH_2[Fe(CO)_2C_5H_5]_2]Cl \cdot H_2O$. N-2-Chloroethylpiperidine reacts with $NaFe(CO)_2C_5H_5$ to give the yellow-orange compound $C_5H_{10}NCH_2CH_2Fe(CO)_2C_5H_5$ with an iron–carbon σ bond. Reaction of 2-chloromethylpyridine with $NaFe(CO)_2C_5H_5$ or $NaW(CO)_3C_5H_5$ gives yellow-orange $NC_5H_4CH_2Fe(CO)_2C_5H_5$ or yellow $NC_5H_4CH_2W(CO)_3C_5H_5$, respectively, with metal–carbon σ bonds. However, reaction of 2-chloromethylpyridine with $NaMn(CO)_5$ or $NaMo(CO)_3C_5H_5$ gives pale yellow $NC_5H_4CH_2COMn(CO)_4$ or yellow $NC_5H_4CH_2COMo(CO)_2C_5H_5$, respectively, with a five-membered heterocyclic ring containing the metal atom, an acyl carbonyl group, a CH_2 group, and one carbon and one nitrogen atom of the pyridine system. Spectroscopic evidence for the proposed structures of these new complexes is presented and discussed.

Introduction

Recently we reported some reactions between metal carbonyl anions and haloalkyl sulfides such as $ClCH_2SCH_3$ and $ClCH_2CH_2SCH_3$.[2,3] In the case of 2-chloroethyl methyl sulfide, $ClCH_2CH_2SCH_3$, these studies led to the discovery of a novel type of heterocyclic acyl derivative exemplified by the manganese carbonyl complex $CH_3SCH_2CH_2COMn(CO)_4$ (I).[4] Characteristic of the structure of the new manganese complex I is the presence of a five-membered chelate-type heterocyclic ring containing the manganese atom, an acyl carbonyl group, two other carbon atoms, and a CH_3S group. One lone pair of the sulfur atom of the CH_3S group is coordinated to the manganese atom.

It appeared reasonable to us that the CH_3S group in the heterocyclic ring of $CH_3SCH_2CH_2COMn(CO)_4$ (I) could be replaced by other groups containing a free electron pair capable of being coordinated to a metal atom and so located that coordination to the metal atom will result in a five- or six-membered ring. One category of such groups are those containing tertiary aminoid nitrogen (*e.g.*, $(CH_3)_2N$) with a lone pair readily capable of coordinating with a transition metal atom. Accordingly, we have investigated reactions between carbonyl anions and chloromethyl and 2-chloroethyl tertiary amines with the haloalkyl groups situated with respect to the nitrogen atom to permit formation of an acyl derivative with a five-membered heterocyclic ring containing the metal atom, an acyl carbonyl group, the amine nitrogen atom, and two other carbon atoms. In this paper, the first of a new series from our laboratory discussing unusual compounds obtained from metal carbonyl derivatives (especially anions) and various organonitrogen compounds such as amines, isocyanates, diazonium salts, etc., we describe compounds prepared from metal carbonyl anions and the three haloalkylamines: (a) 2-chloroethyldi-


I

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[1] Some of this work was presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965; Abstracts, p. 43M.

[2] R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 1267 (1964).

[3] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 486 (1965).

[4] Strictly speaking, an arrow should be drawn from the sulfur atom to the manganese atom in order to indicate the manganese–sulfur bond. This bond is omitted for formulas in the text for I and related compounds for ease in printing the running text.