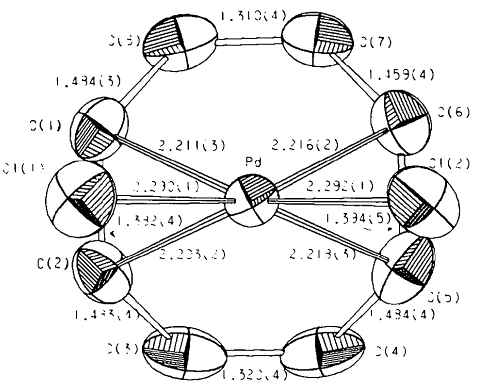

Fig. 1. Plan view of the title compound looking down the bisector of the Cl—Pd—Cl angle.

The structure was solved by Patterson and electron density methods. H atoms were located by difference electron density maps but their parameters were not refined. The function minimized was $R_s = \Sigma w(|F_o| - |F_c|)^2$; the weighted R factor defined by the expression $(R_s/\Sigma wF_o^2)^{1/2}$ was 0·0292. Scattering factors for Pd, C and Cl were from *International Tables for X-ray Crystallography* (1962), those for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion terms were included for Pd and Cl. Positional parameters are given in Table 1,* bond distances and angles in Table 2. A plan view of the molecule is given in Fig. 1, looking down the bisector of the Cl—Pd—Cl angle.

Discussion. The cyclooctatetraene (COT) molecule is very symmetrically coordinated to the Pd atom, the only significant distortion of the cyclooctatetraene molecule being the lengthening of the double bonds which are coordinated to the Pd atom. The bond lengths of the π-coordinated double bonds [1·382 (4), 1·394 (5) Å] are comparable with those found in norbornadienepalladium chloride [1·366 (10) Å] (Baenziger, Richards & Doyle, 1965) and cyclooctatetraenecopper(I) chloride [1·392 (13) Å] (Baenziger, Richards & Doyle, 1964), and can be contrasted with the shorter bond lengths of the uncoordinated double bonds [1·320 (4), 1·310 (4) Å] in the complex and 1·334 (1) Å in the free molecule (Bastiansen, Hedberg & Hedberg, 1957). The single-bond distances in the complex average 1·478 (12) Å, in comparison with 1·462 (1) Å for free COT, 1·48 (1) Å for COT.CuCl and 1·46 (3) Å in COT.$AgNO_3$ (Lipscomb & Mathews, 1959). The ring angles average 122·6 (7)° in the complex, as compared with 126·3 (2)° in free COT.

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Potassium Ethylenediaminetetraacetatomanganate(III) Dihydrate

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Abstract. $KMn(C_{10}H_{12}N_2O_8).2H_2O$, orthorhombic, $P2_12_12_1$, $a = 6·576\ (4)$, $b = 10·038\ (8)$, $c = 23·14\ (2)$ Å, $M_r = 418·3$, $V = 1527·5$ Å^3, $Z = 4$, $D_m = 1·81$, $D_x = 1·82$ g cm^{-3}, μ(Cu $K\alpha$, $\lambda = 1·5418$ Å) $= 103·7$ cm^{-1}.

The Mn atom of the MnY^- complex anion (Y^{4-} ≡ ethylenediaminetetraacetate) is bonded octahedrally to the two N atoms and one O atom from each of the four carboxylate arms of the complexing species. The structure was refined to an *R* of 0·050 for 1020 diffractometer data.

Introduction. The formation of a Mn^{III}–EDTA complex in solution was investigated by Přibil & Horáček (1949). The solid complex has been prepared and characterized by Yoshino, Ouchi, Tsunoda & Kojima (1962). They suggested the formula K[Mn(OH_2)Y].1·5H_2O, and found that the complex was unstable at room temperature and that it suffered decomposition on heating and on exposure to light. The idea of a seven-coordinated Mn^{III} complex with EDTA was next proposed by Hamm & Suwyn (1967) and Boone, Hamm & Hunt (1972), by analogy with the crystallographic establishment by Richards, Pedersen, Silverton & Hoard (1964) that the EDTA complex of Mn^{II} has a seven-coordinated structure. The X-ray analysis presented here has shown the formula of the compound studied to be KMnY.2H_2O.

The title compound was obtained by a method similar to those described by Yoshino, Ouchi, Tsunoda & Kojima (1962). Red crystals grew as flat needles of hexagonal cross-section. In contrast to the earlier results by various authors, the crystalline compound obtained was quite stable in air.

Weissenberg photographs showed that the crystals are orthorhombic; the systematic absences were: $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, $00l$ for $l = 2n + 1$, uniquely indicating the space group $P2_12_12_1$. An irregularly shaped crystal, approximately 0·15 × 0·11 × 0·08 mm, was selected for the data collection. A Syntex $P2_1$ diffractometer and Cu $K\alpha$ radiation with a graphite monochromator were used for lattice-parameter and intensity measurements. The intensities were measured by the θ–2θ scan technique. The intensities of one periodically monitored reflexion

Table 1. *The final positional parameters with standard deviations in parentheses*

Positional parameters are given as fractions of cell edges (×10^4). The H-atom positions (×10^3) are unrefined.

	x	*y*	*z*
Mn	322 (4)	889 (2)	1607 (1)
K	4678 (6)	1535 (3)	4026 (2)
O(1)	1879 (15)	2484 (8)	1684 (4)
O(2)	1678 (17)	337 (8)	869 (3)
O(3)	1285 (15)	389 (8)	2407 (4)
O(4)	−1481 (16)	−588 (7)	1525 (4)
O(11)	2773 (16)	4424 (8)	1307 (4)
O(22)	1315 (17)	133 (9)	−80 (3)
O(33)	1241 (15)	1025 (8)	3329 (3)
O(44)	−4338 (17)	−1558 (9)	1782 (4)
N(1)	−1279 (17)	2113 (9)	950 (4)
N(2)	−2138 (18)	1623 (9)	2149 (4)
C(1)	−65 (22)	3365 (11)	890 (5)
C(2)	−1203 (25)	1308 (13)	422 (4)
C(3)	−1166 (22)	2017 (11)	2685 (5)
C(4)	−3518 (21)	484 (12)	2252 (5)
C(5)	−3359 (23)	2375 (12)	1188 (5)
C(6)	−3208 (21)	2719 (12)	1830 (5)
C(11)	1667 (23)	3477 (12)	1310 (5)
C(22)	786 (23)	528 (12)	390 (5)
C(33)	569 (23)	1068 (10)	2829 (4)
C(44)	−3129 (30)	−654 (13)	1823 (6)
$H_2O(1)$	4642 (18)	3747 (9)	4749 (4)
$H_2O(2)$	8851 (20)	2260 (8)	4146 (4)
H(1)	−100	415	94
H(11)	49	339	48
H(2)	−136	192	7
H(22)	−242	68	42
H(3)	−221	201	301
H(33)	−64	296	265
H(4)	−500	80	220
H(44)	−337	16	266
H(5)	−427	155	113
H(55)	−406	312	96
H(6)	−241	358	188
H(66)	−460	287	201

Table 2. *Bond lengths* (Å) *and angles* (°) *in the* MnY^- *anion*

Mn–N(1)	2·220 (9)	Mn–N(2)	2·176 (10)
Mn–O(1)	1·909 (8)	Mn–O(2)	2·004 (8)
Mn–O(4)	1·907 (8)	Mn–O(3)	2·020 (8)
O(1)–C(11)	1·326 (14)	C(11)–O(11)	1·197 (16)
O(2)–C(22)	1·267 (14)	C(22)–O(22)	1·209 (13)
O(3)–C(33)	1·281 (13)	C(33)–O(33)	1·239 (12)
O(4)–C(44)	1·286 (20)	C(44)–O(44)	1·210 (19)
C(1)–C(11)	1·501 (18)	C(2)–C(22)	1·526 (21)
C(3)–C(33)	1·524 (18)	C(4)–C(44)	1·535 (17)
N(1)–C(1)	1·496 (15)	N(1)–C(2)	1·464 (13)
N(2)–C(3)	1·450 (14)	N(2)–C(4)	1·480 (16)
N(1)–C(5)	1·498 (18)	N(2)–C(6)	1·500 (15)
C(5)–C(6)	1·528 (15)		
N(1)–Mn–N(2)	81·6 (4)	O(1)–Mn–O(2)	94·2 (4)
O(1)–Mn–O(3)	87·4 (4)	O(1)–Mn–O(4)	174·0 (4)
O(2)–Mn–O(3)	125·0 (4)	O(2)–Mn–O(4)	88·7 (4)
O(3)–Mn–O(4)	95·3 (4)	N(1)–Mn–O(1)	81·6 (4)
N(1)–Mn–O(2)	77·3 (4)	N(1)–Mn–O(3)	156·0 (4)
N(1)–Mn–O(4)	93·8 (4)	N(2)–Mn–O(1)	93·5 (4)
N(2)–Mn–O(2)	156·3 (4)	N(2)–Mn–O(3)	77·8 (4)
N(2)–Mn–O(4)	81·9 (4)	Mn–O(1)–C(11)	120·9 (8)
Mn–O(2)–C(22)	119·8 (8)	Mn–O(3)–C(33)	116·9 (8)
Mn–O(4)–C(44)	120·7 (9)	Mn–N(1)–C(1)	106·0 (7)
Mn–N(1)–C(2)	104·4 (7)	Mn–N(1)–C(5)	106·2 (7)
Mn–N(2)–C(3)	105·0 (7)	Mn–N(2)–C(4)	106·7 (7)
Mn–N(2)–C(6)	108·3 (7)	C(1)–N(1)–C(2)	111·7 (9)
C(1)–N(1)–C(5)	111·9 (9)	C(2)–N(1)–C(5)	115·8 (10)
C(3)–N(2)–C(4)	110·0 (9)	C(3)–N(2)–C(6)	115·3 (9)
C(4)–N(2)–C(6)	111·0 (9)	O(1)–C(11)–C(1)	116·5 (11)
O(1)–C(11)–O(11)	122·5 (12)	C(1)–C(11)–O(11)	121·1 (12)
O(2)–C(22)–C(2)	115·6 (11)	O(2)–C(22)–O(22)	127·1 (12)
C(2)–C(22)–O(22)	117·3 (12)	O(3)–C(33)–C(3)	116·1 (10)
O(3)–C(33)–O(33)	124·3 (11)	C(3)–C(33)–O(33)	119·6 (11)
O(4)–C(44)–C(4)	116·7 (12)	O(4)–C(44)–O(44)	123·4 (14)
C(4)–C(44)–O(44)	120·0 (13)	N(1)–C(1)–C(11)	114·1 (10)
N(1)–C(2)–C(22)	110·7 (10)	N(2)–C(3)–C(33)	110·3 (10)
N(2)–C(4)–C(44)	111·6 (10)	N(1)–C(5)–C(6)	109·8 (10)
N(2)–C(6)–C(5)	110·1 (10)		

displayed no observable trend. The data were corrected for Lorentz and polarization effects. Of 1155 accessible reflexions, 1020 with $I > 1{\cdot}96\sigma(I)$ were used for the structure determination. All calculations were performed on a NOVA minicomputer with the Syntex XTL structure determination system. Scattering factors for Mn, K^+, O, N, C and H atoms used were those listed in *International Tables for X-ray Crystallography* (1974); both real and imaginary components of the anomalous dispersion were included for all non-H atoms.

The heavy-atom method was employed for the phase determination. The Mn—Mn vectors were identified in a three-dimensional Patterson function. All non-H atoms were found from several difference-Fourier syntheses. Full-matrix least-squares refinement of the parameters of the two enantiomers (with isotropic thermal parameters) gave R values of 0·074 for one form and 0·112 for the inverted structure. Further refinement with anisotropic thermal parameters for the first enantiomer only gave $R = 0{\cdot}062$. Twelve H atoms from the Y^{4-} anion were placed in geometrically calculated positions at a distance of 1·0 Å from the bonded atoms, and with $B = 3{\cdot}0$ Å^2. Further refinement reduced R to 0·050 and R_w to 0·056. A final three-dimensional difference synthesis was essentially flat and H atoms from water molecules were not resolvable. The final atomic coordinates are listed in Table 1.*

Discussion. The crystals investigated are composed of discrete mononuclear MnY^- anions, K^+ cations and water molecules. The overall structure of the MnY^- anion is similar to that found in the CoY^- anion by Weakliem & Hoard (1959). (The crystallographic system and cell parameters suggested isomorphism of $KMnY.2H_2O$ with $CsCoY.2H_2O$ and $NH_4CoY.2H_2O$.)

The structure of the MnY^- complex anion viewed in projection along **a** is shown in Fig. 1. The Mn atom is bonded octahedrally to two N atoms and to four O atoms from four different carboxylate groups of the complexing molecule. The more important interatomic distances and bond angles are given in Table 2. The average Mn—N distance of 2·20 (3) Å is longer than the Mn—O distances. Furthermore, the Mn—O (opposite the N atoms) bond lengths of 2·01 (1) Å are longer than the Mn—O (*cis* to N atoms) bond lengths of 1·91 (1) Å. The Mn–ligand distances, as well as the ligand–Mn–ligand angles, indicate the distortion from octahedral symmetry required by the Jahn–Teller effect. Comparison of the bond lengths and angles of octahedral Mn^{3+} carboxylate compounds such as $K_3Mn(mal)_3.2H_2O$, $K[Mn(H_2O)_2(mal)_2].2H_2O$ (two modifications) (Lis, Matuszewski & Jeżowska-Trzebiatowska, 1977*a*,*b*), $K_2\{Mn(H_2O)_2[Mn_3O(HCOO)_9]_2\}$ (Lis & Jeżowska-Trzebiatowska, 1977) and $KMnY.2H_2O$ indicates that the distortion from the octahedral configuration is realized in different ways, and not only by the classical model of 'two short and four long' or 'two long and four short' complexing bonds.

The average results of 1·52 (2) Å for C—C and 1·48 (3) Å for C—N and the inter-ring bond angles are in good agreement with the data published for the simpler EDTA complexes. The difference between the chelate ring C—O distances [1·29 (3) Å] and the external C=O distances [1·21 (3) Å] is significant.

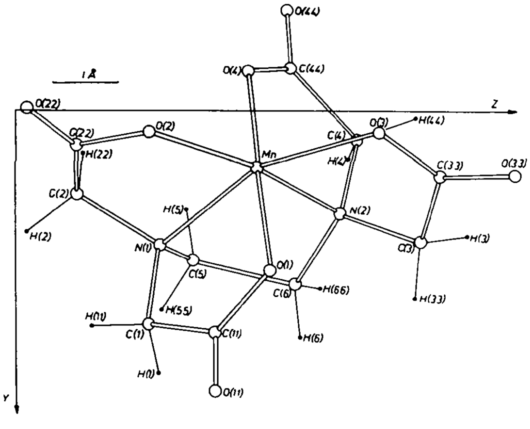

Fig. 1. Structure of the MnY^- anion viewed along the *a* axis of the unit cell.

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