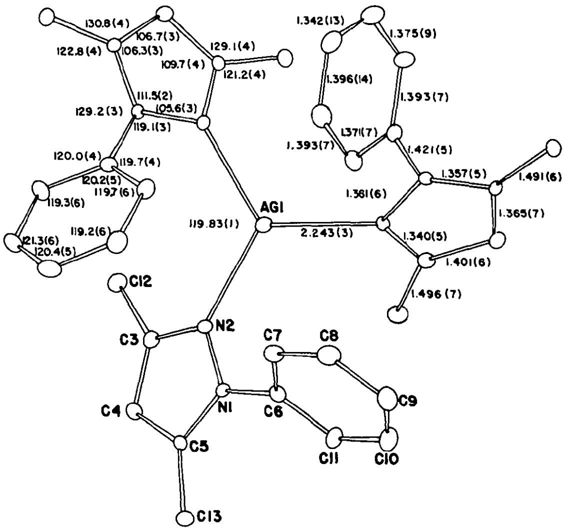

Fig. 1. Diagram of the molecule showing bond lengths (Å) angles (°) and atom numbering.

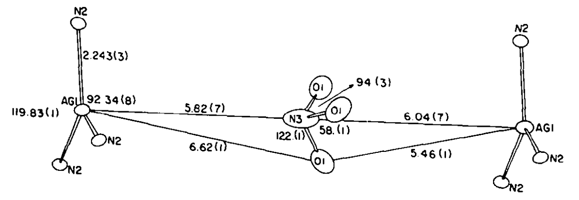

Fig. 2. The relationship of the nitrate group, showing bond distances (Å) and angles (°).

The Ag^+ ion is coordinated to three ligand molecules, $C_{11}H_{12}N_2$. It is at the center of a triangle formed by the N(2) atoms of the pyrazolic rings (Fig. 1). The nitrate group is at about $c/2$ from the heavy atom (Fig. 2). All relevant distances and angles are shown in Figs. 1 and 2. The structure can be described as non-bonded chains of bipyramids running allong the c direction sharing their axial vertices.

As can be seen from the final values of the thermal parameters of the N and O atoms of NO_3^-, this group exhibits much thermal motion [N(3): $U_{11} = U_{22} = 2U_{12} = 0{\cdot}079$, $U_{33} = 0{\cdot}358$, $U_{23} = U_{13} = 0$ Å^2; O(1): $U_{11} = 0{\cdot}151$, $U_{22} = 0{\cdot}157$, $U_{33} = 0{\cdot}152$, $U_{12} = 0{\cdot}087$, $U_{13} = 0{\cdot}027$, $U_{23} = 0{\cdot}045$ Å^2]. The vibration of the N atom is extremely anisotropic with the greatest amplitude along the c direction. This may be due to the large free space left by the organic ligands. The NO_3^- group is not planar and the distance N(3)–O(1) [1·33(3) Å] is longer than the usual value (Addison, Logan & Wallwork, 1971), but similar to one of the N–O distances in $AgNO_3$: 1·19 (6), 1·32 (6), 1·23 (6) Å (Lindley & Woodward, 1966). The deformations and interactions of the nitrate group cannot be checked by infrared spectroscopy because the NO_3^- characteristic bands are masked by typical bands of the organic ligands. All other bond angles and distances are normal.

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Isopropylammonium Trichloromanganate(II) Dihydrate

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Abstract. $(CH_3)_2CHNH_3MnCl_3.2H_2O$, $C_3H_{10}Cl_3Mn$-$N.2H_2O$, monoclinic, $P2_1/c$, $a = 14{\cdot}435$ (14), $b = 5{\cdot}889$ (2), $c = 13{\cdot}281$ (9) Å, $\beta = 109{\cdot}60$ (2)°, $Z = 4$, $D_c = 1{\cdot}607$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å. The structure contains discrete $Mn_2Cl_6(H_2O)_4$ dimers which are hydrogen-bonded together to form a two-dimensional layer in the bc plane. Adjacent layers are separated by the organic cations. Each dimer contains a pair of nearly symmetric Mn–Cl–Mn bridges with a bridging angle of 94·58°. The average Mn–Cl distance is 2·558 Å and the average Mn–O distance is 2·212 Å.

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Introduction. Crystals of $(CH_3)_2CHNH_3MnCl_3.2H_2O$ can easily be grown from aqueous or ethanolic solutions of roughly equal molar mixtures of $(CH_3)_2CHNH_3Cl$ and $MnCl_2.4H_2O$. They grow as flat, rhombic platelets with the characteristic pink coloration of octahedral Mn^{II}.

A small crystal 0·023 × 0·20 × 0·20 mm was mounted for data collection. Systematic extinctions of $l = 2n + 1$ for $h0l$ reflections and $k = 2n + 1$ for $0k0$ reflections determined the space group uniquely as $P2_1/c$ for the monoclinic crystal. Lattice constants were determined by accurately centering 12 reflections with Mo $K\alpha$ radiation. The (100) faces are the large developed faces of the platelets. Intensity data were collected on an automated Picker diffractometer with Zr-filtered Mo $K\alpha$ radiation. A θ–2θ scan of 2·0° was utilized with 20 steps of 3 s duration. Background was counted for 30 s before and after each scan. A total of 1813 independent reflections were collected in the range $2\theta \leq 50°$, of which 1550 had intensity greater than $3\sigma(I)$ where $\sigma^2(I) = \text{TC} + \text{BC} + (0{\cdot}03)^2 I^2$ and TC = total counts, BC = background counts, and I = TC − BC. Absorption corrections were made (μ = 2·20 mm^{-1}).

The structure was solved using conventional heavy-atom Patterson function analysis and electron density/difference electron density maps. The structure refinement proceeded in a straightforward manner and it was possible to locate the H atoms from a difference synthesis. Full-matrix refinement with ansiotropic thermal parameters for all non-hydrogen atoms (but with all H atom parameters fixed) converged to a final conventional R value of 0·043 and a weighted R value of 0·045 [$w(hkl) = 1/\sigma^2(F)$]. The standard deviation of a reflection of unit weight was 2·2.* Scattering factors were taken from *International Tables for Crystallography* (1968). Final structural parameters are given in Table 1 and pertinent interatomic distances and angles in Table 2. Computer programs were part of a local library (Anderson, 1971; Caputo, 1976).

Table 1. *Final positional parameters* (×10^5 *for* Mn *and* Cl; × 10^4 *for* O, N *and* C; × 10^3 *for* H)

	x	*y*	*z*
Mn	12228 (4)	3786 (10)	−2472 (4)
Cl(1)	4358 (7)	18816 (18)	10942 (7)
Cl(2)	27328 (8)	28047 (18)	6261 (8)
Cl(3)	18362 (8)	−13115 (19)	−16177 (8)
O(1)	1772 (2)	−2459 (5)	889 (2)
O(2)	537 (2)	3193 (5)	−1347 (2)
N	2715 (2)	3754 (6)	8023 (2)
C(1)	3802 (3)	4295 (8)	8646 (3)
C(2)	4164 (4)	5971 (9)	8003 (4)
C(3)	4380 (4)	2081 (10)	8885 (4)
HO(11)	153	636	132
HO(12)	194	677	59
HO(21)	41	359	808
HO(22)	37	416	900
HC(11)	380	505	937
HC(21)	364	732	772
HC(22)	422	476	739
HC(23)	483	683	820
HC(31)	431	326	319
HC(32)	395	366	419
HC(33)	525	313	439
HN(1)	257	260	853
HN(2)	255	257	720
HN(3)	260	530	809

Discussion. The crystal structure of $[(CH_3)_2CHNH_3]MnCl_3.2H_2O$ consists of centrosymmetric $Mn_2Cl_6(H_2O)_4$ anionic dimers (Fig. 1) and isopropylammonium cations. Interdimer hydrogen bonds tie the

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *in* $[(CH_3)_2CHNH_3]MnCl_3.2H_2O$

Dimer			
Mn–Cl(1)	2·570 (1)	Cl(1)–Mn–Cl(1)^a	85·43 (4)
Mn–Cl(1)^a	2·639 (1)	Cl(1)–Mn–Cl(2)	90·05 (4)
Mn–Cl(2)	2·538 (1)	Cl(1)–Mn–Cl(3)	174·33 (4)
Mn–Cl(3)	2·484 (1)	Cl(1)^a–Mn–Cl(2)	174·97 (4)
Mn–O(1)	2·213 (3)	Cl(1)^a–Mn–Cl(3)	88·91 (4)
Mn–O(2)	2·211 (3)	Cl(2)–Mn–Cl(3)	95·61 (4)
Mn–Mn	3·828 (1)	O(1)–Mn–Cl(1)	85·87 (9)
		O(1)–Mn–Cl(1)^a	88·63 (9)
		O(1)–Mn–Cl(2)	93·28 (7)
		O(1)–Mn–Cl(3)	93·61 (9)
		O(1)–Mn–O(2)	174·33 (12)
		O(2)–Mn–Cl(1)	89·75 (9)
		O(2)–Mn–Cl(1)^a	87·44 (8)
		O(2)–Mn–Cl(2)	90·32 (8)
		O(2)–Mn–Cl(3)	90·40 (8)
		Mn–Cl(1)–Mn	94·57 (6)
Cation			
N–C(1)	1·542 (5)	N–C(1)–C(2)	108·3 (3)
C(1)–C(2)	1·508 (8)	N–C(1)–C(3)	108·8 (4)
C(1)–C(3)	1·523 (8)	Cl(2)–C(1)–C(3)	114·1 (4)
Hydrogen-bonding contacts			
N–Cl(2)^b	3·321 (3)	C(1)–N–Cl(2)^b	103·7 (2)
N–Cl(3)^c	3·270 (4)	C(1)–N–Cl(3)^c	96·5 (2)
N–Cl(3)^d	3·338 (4)	C(1)–N–Cl(3)^d	118·4 (2)
		Cl(2)^h–N–Cl(3)^c	120·9 (1)
		Cl(2)^b–N–Cl(3)^d	90·9 (1)
		Cl(3)^c–N–Cl(3)^d	126·1 (1)
O(1)–Cl(2)^e	3·186 (3)	Mn–O(1)–Cl(2)^e	131·0 (1)
O(1)–Cl(3)^f	3·360 (3)	Mn–O(1)–Cl(3)^f	136·1 (1)
		Cl(2)^e–O(1)–Cl(3)^f	92·9 (1)
O(2)–Cl(1)^g	3·289 (3)	Mn–O(2)–Cl(1)^g	134·9 (1)
O(2)–Cl(1)^h	3·353 (4)	Mn–O(1)–Cl(1)^a	121·1 (1)
		Cl(1)^g–O(2)–Cl(1)^a	103·9 (1)

Symmetry code: (*a*) $-x,-y,-z$; (*b*) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (*c*) $x, 1+y, 1+z$; (*d*) $x, y, 1+z$; (*e*) $x, -1+y, z$; (*f*) $x, -\frac{1}{2}-y, \frac{1}{2}+z$; (*g*) $-x, 1-y, -z$; (*h*) $x, \frac{1}{2}-y, -\frac{1}{2}+z$.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33952 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

dimers together into a two-dimensional net in the *bc* plane as illustrated in Fig. 2. The cations form hydrogen bonds into this net (Fig. 3) in such a manner as to form an organic sheath above and below the layer. The structure is similar to that of β-$RbMnCl_3.2H_2O$ (Jensen, 1967) and $KMnCl_3.2H_2O$ (Jensen, 1968; Birkelund & Jensen, 1972). These latter salts are triclinic, so all dimers assume a single orientation, in contrast to the results for the monoclinic salt reported here.

Each dimer contains two nearly symmetric Mn—Cl(1)—Mn bridges, with Mn—Cl distances of 2·570 and 2·639 Å and a bridging angle of 94·58°. The terminal Mn—Cl bonds, essentially coplanar with the Mn_2Cl_2 moiety, are considerably shorter at 2·484 and 2·539 Å. The O atoms are *trans* across the coordination sphere, at 2·213 and 2·211 Å. The O(1)—Mn—O(2) angle deviates slightly from linearity (174·3°), the Mn—O bonds being tilted in towards the middle of the dimer.

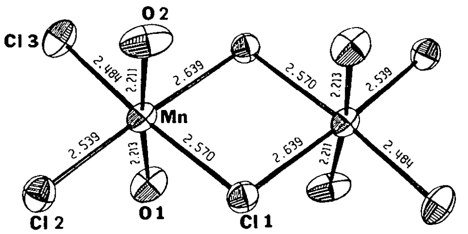

Fig. 1. Geometry of the $Mn_2Cl_6(H_2O)_4$ dimer.

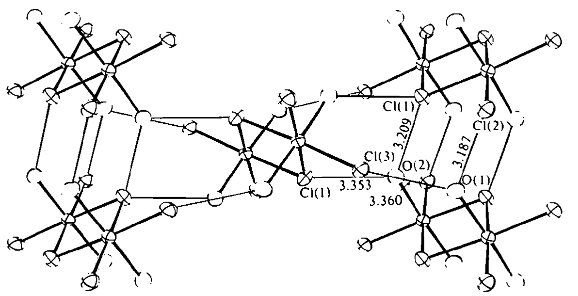

Fig. 2. Illustration of the hydrogen-bonding interactions between dimers. The *b* axis is vertical and the *c* axis horizontal. O atoms are shown without ellipses.

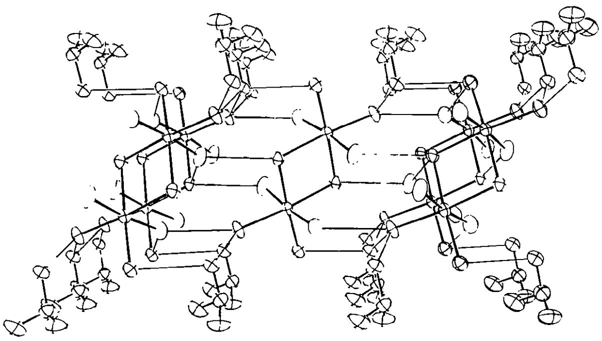

Fig. 3. Illustration of the structure as viewed from the *b* direction. The *c* axis is horizontal. The O atoms are shown without ellipses.

The distortion from idealized D_{2h} symmetry is considerably more severe than that observed in $KMnCl_3.2H_2O$, where the bridging Mn—Cl bond lengths only differ by 0·016 Å and the terminal bond lengths by 0·008 Å. The bridging Mn—Cl—Mn angle is 96·24° in the K salt.

Each water molecule participates in two distinct hydrogen bonds, one with the dimer in the adjacent unit cell in the *b* direction, and one with a dimer diagonally adjacent in the *bc* plane. This is illustrated in Fig. 2, which shows a view onto the *bc* plane. The hydrogen-bond distances between dimers along *b* are shorter (3·187 and 3·209 Å) than those along the *bc* diagonal (3·353 and 3·360 Å). The latter are shown more clearly in Fig. 3, which gives an illustration of the structure as viewed from the *b* direction. In this, it can be seen that these O—H···Cl hydrogen bonds help to hold the network of dimers together. Each N atom is hydrogen bonded to two Cl(3) atoms in adjacent dimers along the *b* axis and to a Cl(2) atom in the dimer diagonally adjacent in the *bc* plane. Thus, the layer of $Mn_2Cl_6(H_2O)_4$ dimers becomes sandwiched between two layers of isopropylammonium ions. These 'sandwiches' stack along the *a* axis, with interlocking of the methyl groups of one sandwich into the gaps between isopropylammonium ions of the adjacent sandwich. It is this packing which determines the β angle of the monoclinic unit cell.

These dimeric structures can be contrasted to two other types of $AMnCl_3.2H_2O$ structures known. $CsMnCl_3.2H_2O$ contains $MnCl_4(H_2O)_2$ octahedra which share corners to form infinite chains (Jensen, Anderson & Rasmussen, 1962). The bridging Mn—Cl—Mn angle is 124·8°. Similar structures are assumed by $(CH_3NH_3)MnCl_3.2H_2O$ and $(CH_3)_2NH_2MnCl_3.2H_2O$ (Caputo, 1976). In $(CH_3)_3NHMnCl_3.2H_2O$ (Caputo, Willett & Muir, 1976) the $MnCl_4(H_2O)_2$ octahedra share edges to form linear chains of stoichiometry $[MnCl_2(H_2O)_2]_n$. The third Cl ion occupies a lattice site independent of the chains. The Mn—Cl—Mn bridging angles are comparable (94·83 and 92·63°) to those in the isopropylammonium dimer. Thus, a variety of structures appear possible for $AMnCl_3.2H_2O$ salts, dictated by packing and hydrogen-bonding interactions.

Since the initial interest in this salt was in its potential magnetic properties, it is worthwhile to point out several features. The magnetic coupling between the Mn^{2+} ions in the dimer is determined principally by the bridging Mn—Cl—Mn angle. The observed angle of 94·58° leads to very weak antiferromagnetic coupling, as evidenced by the results on $(C_5H_5NH)MnCl_3.H_2O$ and $(C_9H_7NH)MnCl_3.H_2O$ (Richards, Quinn & Morosin, 1973; Caputo, Willett & Morosin, 1978) as well as $(CH_3)_3NHMnCl_3.2H_2O$ (Merchant, McClearney, Shankle & Carlin, 1974). All of these linear chain salts contain similar bi-bridged geometries, and the exchange coupling, $2J$, is of the order of $-0·03$ to

$-0{\cdot}05$ mm^{-1}. Exchange coupling *via* hydrogen bonding can be as large or larger, so the system will be expected to behave as a complex two-dimensional magnet, rather than a simple dimer. The isolation of the layers should make this salt a better two-dimensional magnet than the β-$RbMnCl_3.2H_2O$ or $KMnCl_3.2H_2O$ structures. Finally, the Mn^{2+} ions in the dimer are related by centers of inversion. Thus, if the coupling within each dimer is antiferromagnetic as predicted, no spin canting will be present since the spins will be required to align strictly antiparallel by symmetry arguments.

The work was supported by the National Science Foundation.

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Acta Cryst. (1979). B**35**, 181–183

Struktur des Tricarbonyl(trimethyl-1-methoxy-4-oxo-1,2-diphenyl-1,2-diphosphacyclopenten-3,3,5-tricarboxylat)-nickel

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Abstract. $[Ni(C_{22}H_{22}O_8P_2)(CO)_3]$, $C_{25}H_{22}NiO_{11}P_2$, monoclinic, $B2/b$, $a = 36{\cdot}517\ (5)$, $b = 17{\cdot}731\ (5)$, $c = 9{\cdot}380\ (3)$ Å, $\gamma = 91{\cdot}07\ (8)°$, $Z = 8$. The molecule consists of a five-membered ring containing two directly connected P atoms in different oxidation states. The phenyl groups at the P atoms are in *cis* positions relative to each other.

Einleitung. Die von Bergerhoff, Hammes, Falbe, Tihanyi, Weber & Weisheit (1971) erstmals dargestellte Titelverbindung (I) (Fig. 1) lag in nadelförmigen, farblosen, an der Luft und im Röntgenlicht langsam zersetzlichen Kristallen vor. Aus Weissenberg- und Präzessionsaufnahmen folgen die Aussagen über vorhandene Reflexe: hkl nur mit $h + l = 2n$, $hk0$ nur mit $k = 2n$. Die Deutung der dreidimensionalen Patterson-synthese, die mit photometrierten Intensitäten aus integrierten Weissenbergaufnahmen erhalten wurde, gelang jedoch nicht. Dank des Entgegenkommens der Fa. Philips, Eindhoven, stand uns dann für eine Messung kurzfristig das computergesteuerte Zählrohrdiffraktometer PW 1100 zur Verfügung. An einer Kristallnadel (0,2 mm Durchmesser) konnten nun in kürzerer Zeit mit Mo-$K\alpha$-Strahlung (Graphit-Monochromator) bis $2\theta = 36°$ 2089 Reflexe gemessen werden. Aus Patterson- und Fourier-Synthesen konnten jetzt auf dem üblichen Wege nacheinander alle Parameter bis auf die der H-Atome entnommen werden. Alle Rechnungen wurden mit dem XRAY

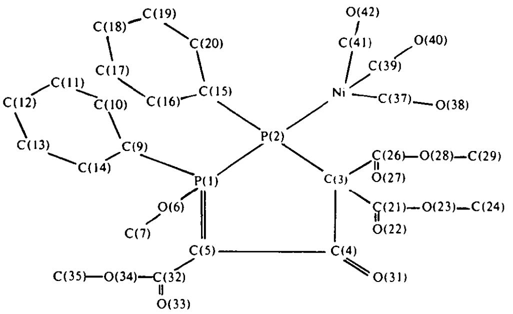

Fig. 1. Bezifferung im Molekül des (I) in Anlehnung an Saenger (1973).

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