Germain, Declercq & Woolfson, 1984) and refined by full-matrix least squares, using the *SHELX*76 program (Sheldrick, 1976). The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = \{\sigma^2(F_o) + \kappa(F_o)^2\}^{-1}$, $\kappa = 0{\cdot}045$ for (I) and 0·0 for (II). f, f' and f'' were taken from *International Tables for X-ray Crystallography* (1974). H atoms were not located.

The final R values were 0·021 ($wR = 0{\cdot}020$) in (I) and 0·020 ($wR = 0{\cdot}020$) in (II) for all observed reflections. Max. and min. peaks in final difference maps were $\pm 0{\cdot}3$ e Å^{-3} at 1·81 Å from Rb for (I) and +0·3, −0·4 e Å^{-3} at 1·69 Å from Cs for (II). Max. shift/e.s.d. = −0·07, U_{22} of O in (I), and −0·08, U_{33} of O in (II).

Discussion. The crystals are isomorphous and contain discrete $[\mathrm{InCl_5(H_2O)}]^{2-}$ distorted octahedra, the In, O and three Cl atoms being positioned on the mirror plane (Fig. 1). Final positional coordinates for $A_2[\mathrm{InCl_5(H_2O)}]$, A = Cs and Rb, are given in Table 1.* Table 2 contains a selection of bond lengths and angles. From the magnitude of the O···Cl distance, it can be stated that in each octahedral unit the O atom is within hydrogen-bonding distance of Cl atoms of neighbouring $[\mathrm{InCl_5(H_2O)}]^{2-}$ octahedra, a fact which is common to the rest of the members in the isomorphic series. Available crystallographic results of isomorphic related compounds are summarized in Table 3.

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trans-Hexakis(pyrazole)manganese(II) Bisperchlorate (1) and *trans*-Dichlorotetrakis(pyrazole)manganese(II) (2)

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Abstract. (1): $[\mathrm{Mn(C_3H_4N_2)_6}](\mathrm{ClO_4})_2$, $M_r = 662{\cdot}31$, trigonal, $P\bar{3}$, $a = 10{\cdot}129\,(4)$, $c = 8{\cdot}039\,(5)$ Å, $V = 714{\cdot}3\,(6)$ Å^3, $Z = 1$, $D_m = 1{\cdot}55\,(2)$, $D_x = 1{\cdot}54$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}73$ mm^{-1}, $F(000) = 339$, $T = 295\,(1)$ K, $R = 0{\cdot}050$ for 577 unique reflections with $I > 3\sigma(I)$. (2): $[\mathrm{MnCl_2(C_3H_4N_2)_4}]$, $M_r = 398{\cdot}16$, monoclinic, $C2/c$, $a = 13{\cdot}695\,(3)$, $b = 9{\cdot}426\,(2)$, $c = 15{\cdot}239\,(2)$ Å, $\beta = 118{\cdot}03\,(1)^\circ$, $V = 1736{\cdot}4\,(5)$ Å^3, $Z = 4$, $D_m = 1{\cdot}57\,(1)$, $D_x = 1{\cdot}52$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}11$ mm^{-1}, $F(000) = 812$, $T = 295\,(1)$ K, $R = 0{\cdot}032$ for 1633 unique reflections with $I > 3\sigma(I)$. The coordination

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sphere about the Mn is octahedral, but in (1) with six N(1)-coordinated pyrazole ligands at distance of 2·261 (4) Å and in (2) with two N(1)- and two N(3)-coordinated pyrazole ligands occupying the equatorial sites at distances 2·249 (2) and 2·229 (2) Å, respectively, and the apical sites occupied by two symmetry-related Cl(1) anions at distance 2·579 (1) Å. In (1) the molecular unit contains two further uncoordinated perchlorate anions in *trans* positions with respect to each other. The neighbouring pyrazole planes are almost orthogonal to (1) or more tilted (2) towards each other and the basal plane. The structures are formed from columns in the **c** directions. There are no hydrogen bonds in the structures. The structures are held together through weak van der Waals forces and loose stacking of parallel pyrazole rings, especially in the column directions.

Introduction. The manganese(II) ion in biological systems has attracted increasing interest in the last few years (Sigel, 1983). Its complexes with heterocyclic ligands, especially those with imidazole and pyrazole and their derivatives, have been studied (Trofimenko, 1972). The structures of only a few of these have been solved so far. Two structures determined recently (Lumme, Lindell & Mutikainen, 1984; Lumme, Lindell & Kivimäki, 1984) are described and compared in the present paper.

Experimental. Crystal data are listed in the *Abstract*. Almost colourless crystals of (1) and (2) were obtained from water. Prismatic crystals of size 0·25 × 0·30 × 0·40 (1) and 0·35 × 0·45 × 0·65 (2) mm were sealed in thin glass (Lindemann) capillaries because of their instability in air during the intensity measurements. Intensities were collected on a Nicolet *P*3*F* automatic diffractometer with graphite-monochromated radiation, using the ω–2θ technique with scan rate varying from $2\theta = 2{\cdot}0$ to $29{\cdot}3°\ \mathrm{min}^{-1}$, depending on the number of counts measured in a fast preliminary scan through the peak. The unit-cell parameters were determined by least-squares treatment of the adjusted angular setting of 16 (1) and 25 (2) reflections. Sets of 843 (1) and 1999 (2) unique reflections were obtained from the 2663 (1) and 2274 (2) reflections measured from $2\theta = 3°$ to the maximum values of 50 (1) and 55° (2), respectively [h: 0,13; k: −13,13; l: −10,10 for (1) and h: 0,18; k: 0,13; l: −20,20 for (2)]. 577 (1) and 1633 (2) reflections with $I > 3\sigma(I)$ were considered as observed and used in the refinement. One (1) and five (2) strong reflections monitored periodically exhibited no significant variation of intensity. The intensities were corrected for Lorentz and polarization effects and for absorption (through the φ-scan technique) for (2) with maximum transmission factor = 1·000 and minimum = 0·730, but corrections for extinction were considered unnecessary.

Table 1. *Atomic coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* (× 10⁴) (*Hamilton,* 1959) *for non*-H *atoms with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$$
$$\simeq\tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	$U_{\rm eq}$(Å²)
Compound (1)				
Mn	0	0	0	467 (11)
N(1)	2095 (5)	1301 (5)	1608 (5)	605 (27)
N(2)	3028 (6)	2829 (6)	1567 (7)	754 (32)
C(1)	4090 (8)	3275 (10)	2767 (10)	906 (49)
C(2)	3846 (8)	2033 (9)	3636 (9)	827 (49)
C(3)	2609 (8)	850 (8)	2875 (8)	772 (44)
Cl(1)	3333	6667	1614 (3)	712 (17)
O(1)	3333	6667	3281 (13)	2109 (70)
O(2)	2057 (8)	5463 (9)	1120 (11)	2286 (78)
Compound (2)				
Mn	2500	2500	5000	404 (3)
N(1)	2409 (2)	2209 (2)	6426 (2)	447 (12)
N(2)	3084 (2)	2792 (3)	7304 (2)	631 (16)
C(1)	2804 (4)	2395 (4)	8024 (2)	737 (23)
C(2)	1923 (4)	1535 (4)	7552 (3)	791 (27)
C(3)	1693 (2)	1430 (3)	6581 (2)	460 (15)
N(3)	3577 (2)	577 (2)	5446 (2)	438 (12)
N(4)	4673 (2)	667 (3)	5995 (2)	598 (15)
C(4)	5136 (3)	−604 (4)	6280 (3)	722 (21)
C(5)	4327 (3)	−1575 (4)	5914 (3)	636 (19)
C(6)	3371 (2)	−794 (3)	5400 (2)	516 (16)
Cl(1)	4243 (1)	4056 (1)	5894 (1)	534 (4)

The structures of (1) and (2) were solved with respect to the heavy atoms by direct methods and developed through successive Fourier syntheses. The refinements were based on F values. With anisotropic temperature factors for non-H atoms, a difference map calculated after full-matrix refinement revealed the positions of the four H atoms for (1) and eight H atoms for (2). Full-matrix least-squares refinement with all non-H atoms anisotropic (and coordinates of Mn restricted) and H atoms isotropic led after four cycles to $R = 0{\cdot}050$ for (1) and after five cycles with H(4) restricted (after the first cycle) to 0·036 for (2), and $wR = 0{\cdot}051$ for (1) and 0·036 for (2), where $w = 1/\sigma(F_o^2)$. After the last cycle $(\Delta/\sigma)_{\rm ave} = 0{\cdot}00015$ for (1) and 0·01817 for (2), and $(\Delta/\sigma)_{\rm max} = 0{\cdot}001324$ for (1) and 0·3818 for (2), respectively. Maximum and minimum heights in final difference Fourier syntheses were +0·51 and −0·51 for (1) and +0·30 and $-0{\cdot}30\ \mathrm{e\ Å^{-3}}$ for (2), respectively. The S values were 2·56 and 12·00 for (1) and (2), respectively.

Scattering factors were from Cromer & Mann (1968) and an anomalous-dispersion correction was applied (*International Tables for X-ray Crystallography,* 1974). All calculations were performed on a UNIVAC 1100/61 E1 computer with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); for planes the program *MPLN* by Truter & Vickery (1973) was used. Densities of the crystals were determined by the flotation method in toluene–CCl_4 (1) and $CHCl_3$–CCl_4

(2) mixtures, respectively. The final atomic parameters are given in Table 1.*

Discussion. Fig. 1 shows the coordination spheres around the Mn^{II} atom in both complexes (1) and (2) with the atom numbering. (1) has one and (2) four molecules in the unit cell. Bond lengths and angles for non-H atoms are listed in Table 2.

The pyrazole rings of both compounds are essentially planar. The deviations from the mean planes defined by the five atoms N(1), N(2), C(1), C(2) and C(3) and N(3), N(4), C(4), C(5) and C(6) are listed in Table 3. The deviations of the five atoms from both rings are within 0·006 (6) Å. The angles between the pyrazole rings and the *ab, ac* and *bc* planes (in direct space) are 128·5 (2), 97·0 (3) and 52·5 (2) for (1) and 103·0 (1) and 34·1 (1), 37·9 (1) and 86·2 (1), and 127·6 (1) and 95·8 (1)° for (2), respectively.

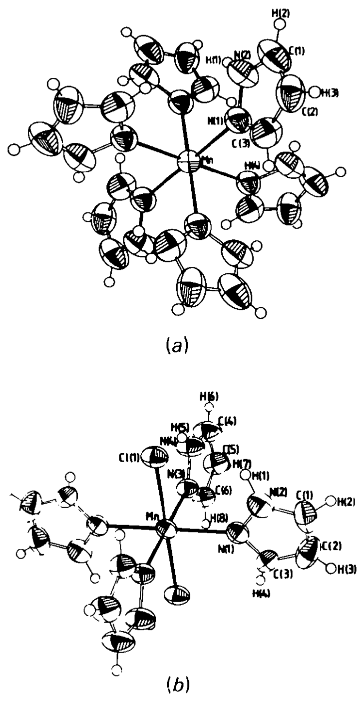

Fig. 1. *ORTEP* (Johnson, 1965) drawings with atomic numbering. (*a*) Compound (1); (*b*) compound (2). The thermal ellipsoids for non-H atoms are drawn at 50% probability.

Table 2. *Interatomic distances* (Å) *and angles* (°) *involving non-*H *atoms with e.s.d.'s in parentheses*

X_{ap}	(1) N(1)	(2) Cl
Mn–X_{ap}	2·261 (4)	2·579 (1)
Mn–N(1)	—	2·251 (3)
Mn–N(3)	—	2·232 (2)
N(1)–N(2)	1·351 (6)	1·336 (3)
N(2)–C(1)	1·344 (9)	1·373 (6)
C(1)–C(2)	1·349 (13)	1·346 (6)
C(2)–C(3)	1·370 (9)	1·364 (6)
C(3)–N(1)	1·325 (10)	1·331 (4)
Cl–O(1)	1·318 (11)	—
Cl–O(2)	1·325 (6)	—
Cl–O(2^i),Cl–O(2^{ii})	1·325 (6)	—
N(3)–N(4)	—	1·334 (3)
N(4)–C(4)	—	1·330 (4)
C(4)–C(5)	—	1·341 (5)
C(5)–C(6)	—	1·381 (4)
C(6)–N(3)	—	1·318 (4)
N(1)–Mn–N(1^{iii})	90·6 (2)	—
Mn–N(1)–C(3)	130·9 (4)	128·1 (2)
Mn–N(1)–N(2)	124·7 (4)	126·2 (2)
N(1)–N(2)–C(1)	110·6 (6)	111·5 (3)
N(2)–C(1)–C(2)	108·4 (6)	104·7 (4)
C(1)–C(2)–C(3)	104·2 (7)	108·4 (5)
C(2)–C(3)–N(1)	112·8 (7)	109·8 (3)
C(3)–N(1)–N(2)	104·1 (5)	105·7 (3)
O(1)–Cl(1)–O(2)	108·4 (4)	—
N(1)–Mn–Cl(1)	—	90·95 (6)
Mn–N(3)–C(6)	—	133·3 (2)
Mn–N(3)–N(4)	—	121·8 (2)
N(3)–N(4)–C(4)	—	111·8 (2)
N(4)–C(4)–C(5)	—	107·7 (3)
C(4)–C(5)–C(6)	—	104·5 (3)
C(5)–C(6)–N(3)	—	111·7 (3)
C(6)–N(3)–N(4)	—	104·2 (2)

Compound (1), symmetry code: (i) $-y+1,\ x-y+1,\ z$; (ii) $-x+y,\ -x+1,\ z$; (iii) $-x,\ x-y,\ z$.

Table 3. *The deviations* (Å) *from the mean planes of the pyrazole rings in direct space with e.s.d.'s in parentheses*

	N(1)	N(2)	C(1)	C(2)	C(3)
Compound (1)	0·004 (6)	–0·006 (6)	0·005 (9)	–0·008 (8)	–0·001 (8)
(2)	0·001 (3)	–0·001 (3)	0·000 (4)	0·001 (4)	–0·001 (3)

	N(3)	N(4)	C(4)	C(5)	C(6)
(2)	–0·0001 (3)	0·001 (3)	–0·001 (4)	0·000 (4)	0·000 (3)

In compound (1) the perchlorate ion is a slightly distorted tetrahedron (Table 2). It may be considered also as a trigonal pyramid with the three oxygen atoms O(2), O(2^i) and O(2^{ii}) forming the base plane from which Cl(1) and O(1) are at distances 0·419 (6) and 1·736 (12) Å (in the **c** direction), respectively. The perchlorate ions form columns in the **c** direction.

The coordination sphere around the manganese(II) ion is a distorted octahedron in both complexes (Table 2). This is formed through six pyrazole rings for (1) and through four pyrazole rings and two Cl atoms for (2), respectively. In (1) the dihedral angles around the central metal atom are 90° within 0·5 (1)° [89·4 (2) and 90·6 (2)°], which is also the angle between the planes of the neighbouring pyrazole rings. In (2) the

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* Lists of structure factors, anisotropic temperature factors for non-H atoms, fractional atomic coordinates, isotropic temperature factors, bond distances and angles of H atoms and most significant planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44721 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

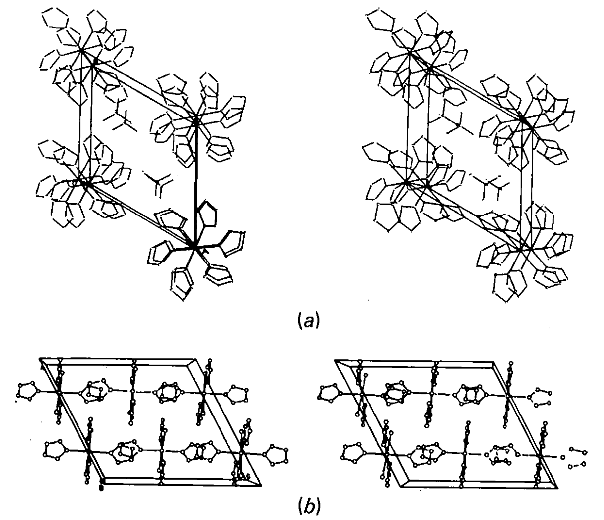

Fig. 2. Stereoscopic views of the crystal structures. (*a*) Compound (1) down **c**; (*b*) compound (2) down **b**.

dihedral angles are 89·1 (1) and 90·9 (1)°, respectively. This shows that the Cl atoms may take the apical positions in the coordination sphere more easily than the perchlorate anions.

The crystal structures are shown in Fig. 2. The structure of (1) is isostructural with that of hexakis(pyrazole)Ni^{II} nitrate (Reimann, Santoro & Mighell, 1970), whereas (2) is isostructural with the corresponding copper(II) (Mighell, Santoro, Prince & Reimann, 1975) and nickel(II) (Reimann, Mighell & Mauer, 1967) complexes. There are no contacts X(—H)···Y, where X = C or N and Y = O or Cl, less than the sum of the van der Waals radii (Taylor & Kennard, 1982) in these crystal structures. Therefore there are no hydrogen bonds, but the structures are held together through weak van der Waals interactions.

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The Structure of $[Au\text{-}\mu\text{-}\{3,5\text{-}(C_6H_5)_2C_3HN_2\}]_3Cl_2$: a Trinuclear Mixed-Valence Gold Pyrazolate Complex

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Abstract. Tris-μ-(3,5-diphenyl-1-pyrazolyl-N,N')-dichlorogold(III)digold(I), M_r = 1319·2, monoclinic, $P2_1/c$, a = 16·477 (3), b = 9·626 (2), c = 25·686 (4) Å, β = 91·16 (1)°, V = 4073 (1) Å^3, D_x = 2·15 Mg m^{-3}, Z = 4, μ = 10·93 mm^{-1}, λ(Mo $K\alpha$) = 0·71073 Å, $F(000)$ = 2464, T = 298 K. The structure consists of a discrete trinuclear gold pyrazolate molecule containing a four-coordinate gold(III) center with *trans* chloride ligands and two two-coordinate gold(I) centers. The Au atoms are symmetrically bridged by the pyrazolate

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