O*W*(2) and O*W*(3)], two O atoms [O(7) and O(8)] of carbonyl ligands which do not participate in hydrogen bonding with the water molecules, and the carbonyl O(5) atom hydrogen bonded with atom O*W*(3) (Fig. 2 and Table 2).

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Structure of Bis(tetramethylammonium) Hexachlororhenate(IV)

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Abstract. Bis(tetramethylammonium) hexachlororhenate(IV), $[N(CH_3)_4]_2[ReCl_6]$, $M_r = 547.2$, cubic, $Fm3m$, $a = 12.760\,(2)$ Å, $V = 2077.5\,(6)$ Å^3, $Z = 4$, $D_x = 1.7505\,(6)$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 75.0$ cm^{-1}, $F(000) = 1052$. The structure was solved by Patterson and difference Fourier methods and refined to an R value of 0.0669 against 176 unique reflections collected at room temperature. Structural parameters are discussed and compared with those derived from other hexachlororhenate complexes.

Introduction. The low-temperature laser-excited luminescence spectra of the related series of compounds A_2ReCl_6 [A = K, Rb, Cs, $N(CH_3)_4$, $N(C_2H_5)_4$] have been reported and discussed (Bettinelli, Flint & Ingletto, 1991). The well resolved spectra have been assigned to the $\Gamma_7(^2T_{29}) \rightarrow \Gamma_8(^4A_{29})$ transition in several defect sites of essentially octahedral geometry. The emitting traps have been identified as $ReCl_6^{2-}$ ions at elongated lattice sites near interstitial sites or dislocations.

Single-crystal X-ray data (Grundy & Brown, 1970; Sperka & Mautner, 1988) showed that the alkali-metal salts K_2ReCl_6 and Cs_2ReCl_6 are cubic (space group $Fm3m$) and that the regular $ReCl_6^{2-}$ ions occupy sites of perfect octahedral symmetry. The luminescence spectra of K_2ReCl_6, Rb_2ReCl_6 and Cs_2ReCl_6 are characterized by vanishingly small electronic origins and strong vibronic origins, indicating that the defect sites maintain the inversion symmetry of the regular sites. $[N(C_2H_5)_4]_2ReCl_6$ has been shown by single-crystal X-ray diffraction (Bettinelli, Di Sipio, Valle, Aschieri & Ingletto, 1989) to be isostructural with $[N(C_2H_5)_4]_2SnCl_6$ (monoclinic, space group $C2/c$) with $ReCl_6^{2-}$ sites of C_1 symmetry, only slightly distorted from O_h. The luminescence spectra of this compound are dominated by pure

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electronic origins accompanied by much weaker vibronic origins, indicating that the emitting centres have no centre of inversion and are therefore less symmetric than the regular sites. The different behaviour, with respect to the alkali-metal salts, can be ascribed to the distorted symmetry of the lattice of $[N(C_2H_5)_4]_2SnCl_6$, which results in the defect lattice sites near interstitial sites or dislocations being non-centrosymmetric. The distortion is attributed to the bulky cations.

The luminescence spectra of $[N(CH_3)_4]_2ReCl_6$ are similar to those of the tetraethylammonium salt and show strong zero-phonon electronic origins; the emitting traps occupy sites lacking the centre of inversion. It would be interesting to correlate the symmetry of the defect sites and molecular structure of $[N(CH_3)_4]_2ReCl_6$. However, detailed structural information for this compound is missing. In an old study (Bagnall, Brown & Coolton, 1964), powder diffraction data suggested a cubic structure (space group *Fm*3*m*), but a single-crystal analysis is lacking. Moreover, the powder data do not seem to be consistent with the fact that the structures of the similar compounds $[N(CH_3)_4]_2SnCl_6$ and $[N(CH_3)_4]_2ReBr_6$ have been refined in the space groups *Fd*3*c* (cubic) (Nielsen & Berg, 1980) and *I*4$_1$/*acd* (tetragonal) (Drück, 1972), respectively. For these reasons, we report in this paper the complete structural determination of the title compound.

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* (Å^2) *for the non-*H *atoms with e.s.d's in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	*y*	*z*	U_{eq}
Re	0.0	0.0	0.0	0.041 (1)
Cl	0.1850 (10)	0.0	0.0	0.094 (23)
N	0.25	0.25	0.25	0.044 (19)
C	0.3142 (28)	0.3142 (28)	0.3142 (28)	0.150 (28)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Re—Cl	2.360 (3)	Cl—Re—Cl	90
N—C	1.419 (29)	C—N—C	109.5
C—H	1.080 (41)	H—C—H	109.5

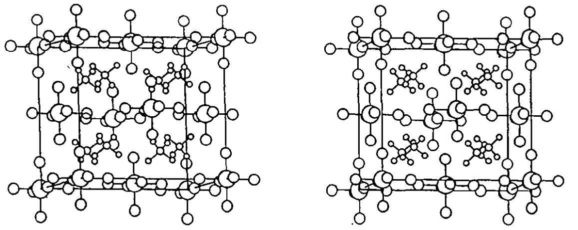

Fig. 1. Stereoview of the molecular packing of bis(tetramethylammonium) hexachlororhenate(IV) viewed along the *a* axis. The Re, Cl, N and C atoms are shown as circles of decreasing size and H atoms are omitted for clarity.

Expermental. Small single crystals of $[N(CH_3)_4]_2ReCl_6$ were grown by solvent evaporation from a dilute solution containing stoichiometric quantities of $[N(CH_3)_4]Cl$ (EGA-Chemie Reagent Grade) and K_2ReCl_6 (Alfa Ventron Reagent Grade) in 2 mol dm^{-3} aqueous HCl. The C, H and N elemental analyses were in agreement with the expected stoichiometry. A light-green prismatic crystal with dimensions 0.23 × 0.23 × 0.48 mm was used for data collection. Intensity data were collected at room temperature on an Enraf–Nonius FAST diffractometer using Mo $K\alpha$ radiation. One hemisphere of data was collected with a detector swing angle of 18° and a crystal-to-detector distance of 40 mm. This corresponds to a minimum θ_{max} value of 24°. Additional data with a non-spherical distribution, owing to the geometry of the 'flat plate' system, were also collected and included ($0 < h < 9$; $0 < k < 12$; $0 < l < 17$). Three standard reflections showed no significant variations during data collection. Data were corrected for Lorentz–polarization factors and absorption. Unit-cell dimensions were refined using a least-squares fit on the positions of 25 high-angle reflections ($23 < 2\theta < 28°$). Autoindexing suggested the crystals were tetragonal but the refined unit-cell parameters *a* and *c* were related by a factor $2^{1/2}$, suggesting cubic symmetry. Transformation of the indexed data to the new cubic cell and remerging confirmed this observation. The space group (*Fm*3*m*) was determined from the systematic absences ($h + k$, $k + l$, $h + l = 2n$) and confirmed by structure analysis.

Merging a total of 4662 equivalent reflections gave 185 unique intensities with $R_{int} = 0.046$; 176 intensities had $I > 3\sigma(I)$. The structure was solved by Patterson and difference Fourier methods and refined by full-matrix least-squares refinement of the structure-factor amplitudes, anisotropic for non-H atoms using *SHELX76* (Sheldrick, 1976), to a crystallographic residual $R = 0.066$, R (all data) = 0.088, $wR = 0.059$ and max. (shift/σ) = 0.0289. The function minimized was $w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(|F_o|)]^{-1}$. H atoms were placed in calculated positions and included in the final structure-factor calculation with isotropic thermal parameters. The atomic scattering factors used were taken from *SHELX76* and *International Tables for X-ray Crystallography* (1974, Vol. IV). The final difference map showed no significant features, the maximum and minimum electron densities being 0.50 and −0.47 e Å^{-3}, respectively. All calculations were carried out on a VAX 3300 computer. Geometrical calculations were performed with *XANADU* (Roberts & Sheldrick, 1979). Molecular illustrations were drawn using the interactive graphics package *FRODO* (Jones, 1985).

Discussion. The refined atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms are given in Table 1.* Distances and bond angles are listed in Table 2. The crystals are isostructural to those of $[N(CH_3)_4]_2SnCl_6$ determined by Berg & Sotofte (1978). The Re, N and Cl atoms occupy special positions in the crystal. A stereoview of the crystal packing is shown in Fig. 1. The shortest Re···Re interatomic distances are 9.023 (2) Å (12 neighbours) and 12.760 (2) Å (6 neighbours). These fall between the comparable distances for $[N(C_2H_6)_4]_2ReCl_6$ and the alkali-metal salts K_2ReCl_6 and Cs_2ReCl_6 (Grundy & Brown, 1970; Bettinelli, Di Sipio, Valle, Aschieri & Ingletto, 1989). The Cl atoms occupy octahedral positions around the central Re atom, the Cl—Re—Cl angles being exactly 90°. In all other hexachlororhenates, although crystallographically significant, these angles only marginally deviate from 90°. The Re—Cl distance of 2.360 (2) Å also correlates well with other literature values.

The high temperature factors of the tetramethylammonium counterion indicate a thermal rigid-body motion around the central N atom similar to that reported for $[N(CH_3)_4]_2SnCl_6$ by Nielsen & Berg (1980). The reason for this rotational disorder compared with the other ammonium salts of hexachlororhenate may be due to a lack of hydrogen-bonding potential between the Cl atoms and the counterion.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55444 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1000]

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Structure of Hexa-μ-acetato-$1\kappa^3O$:$2\kappa^3O'$;$2\kappa^3O$:$3\kappa^3O'$-bis(1,10-phenanthroline)-$1\kappa^2N^1$,N^{10};$2\kappa^2N^1$,N^{10}-trimanganese(II)

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Abstract. $[Mn_3(C_2H_3O_2)_6(C_{12}H_8N_2)_2]$, $M_r = 879.5$, monoclinic, $A2/a$, $a = 26.414$ (3), $b = 12.433$ (2), $c = 11.410$ (2) Å, $\beta = 98.63$ (2)°, $V = 3704.7$ (10) Å^3, $Z = 4$, $D_m = 1.576$, $D_x = 1.576$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.032$ mm^{-1}, $F(000) = 1796$, $T = 298$ K, $R = 0.073$ and $wR = 0.063$ for 2142 observed reflections. In the linear trinuclear compound, one of the Mn atoms is on the twofold axis and is coordinated by six O atoms of the acetate ions with an average Mn—O distance of 2.131 (8) Å. The other

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