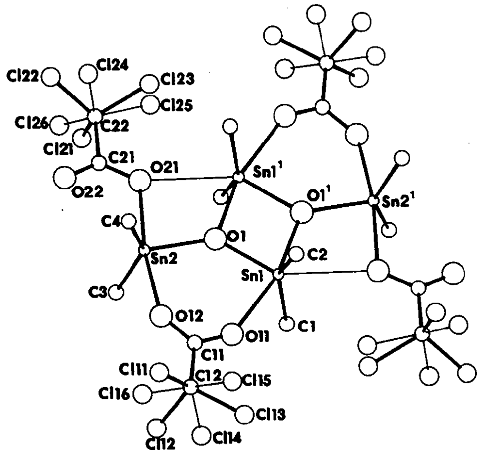

Fig. 1. The molecular structure of di-μ_3-oxo-bis(μ-trichloroacetato-*O,O'*)-bis(trichloroacetato)tetrakis[dimethyltin(IV)]. The H atoms have been omitted for clarity. The asymmetric unit bears the numbering scheme.

axial Sn—O bonds are slightly longer (mean Sn—O = 2·21 Å). Although the Sn-atom environments are similar, the trichloroacetate ions are quite different. One forms a symmetrical bridge between Sn(1) and Sn(2), mean Sn—O = 2·235 Å. The other is bonded only to Sn(2) [Sn(2)—O(21) = 2·262 Å] making the ion very asymmetric. O(21) also forms a very weak bond to Sn(1^i), Sn(1^i)···O(21) = 2·70 Å. The other O atom of this ion, O(22), forms a weak bond to Sn(2^i) in the adjacent dimer [Sn(2^i)···O(22) = 3·09 Å] linking the independent molecules into a ladder-type structure running along the *a* axis.

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Structure of Bis(2,2′,2″-triaminotriethylamine-*N,N′,N″*)-μ-(triethylenetetramine-*N,N′,N″,N‴*)-dinickel(II) Tetraperchlorate

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Abstract. μ-[2,2′-(Ethylenediamino)di(ethylamine)-*N,N′,N″,N‴*]-bis(2,2′,2″-nitrilotriethylamine)dinickel(II) tetraperchlorate, $[Ni_2(C_6H_{18}N_4)(C_6H_{18}N_4)_2]$-$(ClO_4)_4$, M_r=954·0, monoclinic, $C2/c$, a=20·285(4), b = 18·112 (4), c = 15·045 (3) Å, β = 135·70 (1)°, V = 3861 (3) Å^3, Z = 4, D_x = 1·63 g cm^{-1}, Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 13·33 cm^{-1}, $F(000)$ = 1992, T = 293 K, R = 0·042, wR = 0·043, 1564 unique reflections. The structure consists of pairs of octahedrally coordinated Ni^{II} ions and isolated perchlorate ions. Each tren ligand (tren ≡ 2,2′,2″-triaminotriethylamine) occupies four coordination sites on each Ni^{II} ion, spanning a pair of adjacent octahedral faces. The trien ligand (trien ≡ triethylenetetramine) bridges between two Ni ions, with two N atoms coordinating in a *cis* fashion to each Ni atom, completing the Ni coordination spheres.

Introduction. The system Ni^{II}–tren has been the subject of several kinetic studies in solution, including the rate of water exchange in the aqua complex (Rablen, Dodgen & Hunt, 1972) and substitution of water by ammonia (Jones, Billo & Margerum, 1970). In the water exchange study, two different exchange rates were observed, leading the authors to propose a *cis*-octahedral arrangement for the $Ni(tren)(H_2O)_2^{2+}$ species. Other authors have suggested tetrahedral (Bertsch, Fernelius & Block, 1958) or trigonal bipyramidal (Jonassen & Thilemann, 1963). In this paper, we present solid-state structural results for the compound bis(triaminoethylamine)(triethylenetetramine)dinickel(II) perchlorate, $C_{18}H_{54}N_{12}Ni_2^{4+}.4ClO_4^-$ (I), supporting the concept of a *cis*-octahedral arrangement. During an earlier period, we attempted to solve the structure, but were unsuccessful. In order to

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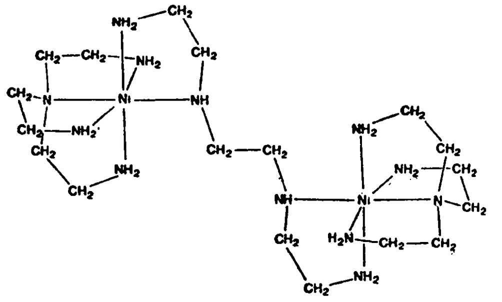
test the software with our new Nicolet *R*3*m*/*E* diffractometer system, we collected a new data set and proceeded with the structural analyses.



(I)

Experimental. Crystals were obtained from an NMR sample tube containing an aqueous solution of $Ni(ClO_4)_2$ and tren that had partially evaporated. A section of a small needle (~0·1 × 0·1 × 0·1 mm) was selected for data collection (Campana, Shepherd & Litchman, 1980) on a Nicolet *R*3*m*/*E* diffractometer. Lattice parameters determined from the accurate centering of 25 reflections with $30 < 2\theta < 37°$. Two octants (h, $k \geq 0$) were collected using a θ–2θ scan. Three standards ($31\bar{4}$; 112; $22\bar{3}$) were monitored every 50 reflections and showed no systematic variation. $R_{\rm int} = 0{\cdot}0178$. No absorption corrections were made. 1564 unique reflections were collected ($2\theta \leq 40°$, $h \leq 18$, $k \leq 16$, $-12 \leq l \leq 12$) of which 1277 had intensity greater than $3\sigma(I)$. The structure solution was obtained through the *SHELXTL* automatic interpretation of the Patterson function to yield the Ni^{II}-ion position, followed by subsequent cycles of structure-factor calculation and difference syntheses to locate the other atoms. Final refinement on F included rigid-body refinement of H-atom positions ($r_{\rm C-H} = r_{\rm N-H} = 0{\cdot}96$ Å) with thermal parameters set at approximately 20% larger than the heavy atom to which each H atom was bonded. Final refinement for the observed data set led to $R = 0{\cdot}042$ and $wR = 0{\cdot}043$ with $w = 1/[\sigma^2(F) + gF^2]$ with $g = 0{\cdot}0053$ and the goodness of fit = 1·56. Extinction corrections were not applied, since examination of the largest $|\Delta F/\sigma|$ values revealed no evidence for extinction effects. Final positional parameters are given in Table 1 with bond distances and angles in Table 2.* The maximum residual electron density was approximately 0·5 e Å^{-3} in the vicinity of Cl(1). The minimum residual density was –0·3 e Å^{-3}. Av. $|\Delta/\sigma| = 0{\cdot}070$, max. $|\Delta/\sigma| = 0{\cdot}377$ on last cycle of least squares. The 1984 *SHELXTL* programs (Sheldrick, 1984) were used for all data reduction, structure solution and refinement and graphics. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Table 1. *Atomic coordinates* (×10⁴) *and isotropic thermal parameters* (Å² × 10³)

	x	y	z	U*
Ni	2232 (1)	3849 (1)	7010 (1)	31 (1)
N(2)	2408 (4)	3362 (3)	5894 (5)	43 (5)
C(2)	3113 (5)	2759 (4)	6627 (6)	54 (7)
C(1)	3776 (4)	2894 (4)	8044 (6)	58 (7)
N(1)	3241 (4)	3064 (3)	8340 (5)	43 (5)
C(3)	2776 (6)	2388 (4)	8245 (7)	66 (8)
C(4)	1786 (6)	2472 (4)	7513 (9)	84 (10)
N(3)	1294 (4)	2983 (3)	6463 (5)	48 (5)
C(5)	3830 (5)	3448 (4)	9580 (7)	65 (7)
C(6)	3214 (5)	3777 (4)	9721 (6)	67 (8)
N(4)	2422 (4)	4195 (3)	8553 (5)	46 (5)
N(12)	1184 (3)	4657 (3)	5674 (5)	34 (4)
N(11)	3166 (4)	4715 (3)	7469 (5)	42 (5)
C(12)	2575 (4)	5236 (4)	6383 (7)	47 (6)
C(11)	1664 (5)	5369 (3)	5985 (7)	47 (7)
C(13)	371 (4)	4727 (3)	5506 (6)	41 (6)
Cl(1)	3866 (1)	5962 (1)	10233 (2)	60 (2)
O(11)	4072 (4)	6732 (3)	10477 (7)	106 (7)
O(12)	4551 (5)	5543 (4)	10476 (7)	125 (9)
O(13)	3717 (7)	5685 (4)	10942 (9)	153 (12)
O(14)	2994 (5)	5860 (4)	8999 (7)	173 (8)
Cl(2)	0	6744 (2)	2500	67 (3)
O(21)	−183 (8)	6683 (7)	1437 (10)	93 (11)
O(23)	1031 (8)	6594 (9)	3602 (11)	128 (13)
O(24)	483 (11)	6283 (7)	2417 (17)	153 (24)
O(22)	0	7516 (6)	2500	174 (17)
Cl(3)	0	3909 (2)	2500	75 (3)
O(31)	5151 (5)	8480 (4)	3399 (6)	137 (7)
O(32)	4211 (5)	9366 (4)	1811 (6)	146 (8)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Discussion. The cation is a binuclear species consisting of two Ni^{II} ions, two tren ligands, and one trien ligand (Fig. 1). The trien ligand is present as a substantial impurity in commercial tren samples. Each Ni^{II} ion has one tren ligand capping two adjacent faces of its coordination octahedron, with a terminal ethylenediamine arm of the trien ligand completing the coordination sphere. The ethylenediamine arms of the tren and trien ligands cause considerable contraction of the bidentate N—Ni—N angle (range 81·8–82·6°) from their ideal 90° values. Otherwise, the tren ligand is able to adapt to the octahedral stereochemistry without severe distortion. The C—N(1)—C angles at the apical N atom are only slightly greater than the ideal tetrahedral angles (range 110·8–113·1°) and the Ni—N(1)—C bond angles are generally somewhat less (range 103·9–110·4°). However, the Ni—N(1) bond is shortened considerably (2·087 Å) compared to the other Ni—N bonds (2·143 Å average) in order to accommodate the ligand. The trien ligand, unusual in its bridging nature, is otherwise unremarkable in its behavior. It assumes a nearly planar conformation with

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* Anisotropic thermal parameters, H-atom positions and a listing of observed and calculated structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43888 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

a center of inversion at the middle of the central C(13)—C(13′) bond. Indeed, the largest strain seems to be in that central linkage, with both the Ni—N(12)—C(13) angle (117·0°) and the N(12)—C(13)—C(13′) angle (114·4°) significantly larger than ideal tetrahedral values.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and hydrogen-bonding contacts* < 3·3 Å

Ni—N(2)	2·140 (9)	Ni—N(1)	2·087 (5)
Ni—N(3)	2·125 (6)	Ni—N(4)	2·156 (18)
Ni—N(12)	2·141 (4)	Ni—N(11)	2·158 (6)
N(2)—C(2)	1·482 (8)	C(2)—C(1)	1·520 (11)
C(1)—N(1)	1·471 (15)	N(1)—C(3)	1·489 (12)
N(1)—C(5)	1·484 (10)	C(3)—C(4)	1·450 (14)
C(4)—N(3)	1·446 (11)	C(5)—C(6)	1·530 (18)
C(6)—N(4)	1·484 (7)	N(12)—C(11)	1·475 (8)
N(12)—C(13)	1·485 (13)	N(11)—C(12)	1·480 (8)
C(12)—C(11)	1·499 (14)	C(13)—C(13′)	1·510 (11)
Cl(1)—O(11)	1·427 (6)	Cl(1)—O(12)	1·384 (10)
Cl(1)—O(13)	1·393 (17)	Cl(1)—O(14)	1·381 (6)
Cl(2)—O(21)	1·364 (17)	Cl(2)—O(23)	1·495 (11)
Cl(2)—O(24)	1·359 (24)	Cl(2)—O(22)	1·399 (12)
Cl(2)—O(21*a*)	1·364 (17)	Cl(2)—O(23*a*)	1·495 (11)
Cl(2)—O(24*a*)	1·359 (24)	O(21)—O(24)	1·293 (16)
O(21)—O(23*a*)	1·688 (28)	O(23)—O(24)	1·377 (24)
O(23)—O(21*a*)	1·688 (28)	Cl(3)—O(31*a*)	1·390 (10)
Cl(3)—O(31*b*)	1·390 (10)	Cl(3)—O(32*a*)	1·395 (9)
Cl(3)—O(32*b*)	1·395 (9)	O(31)—Cl(3*a*)	1·390 (10)
O(32)—Cl(3*a*)	1·395 (9)		

N(2)—Ni—N(1)	82·6 (3)	N(2)—Ni—N(3)	89·8 (3)
N(1)—Ni—N(3)	81·9 (2)	N(2)—Ni—N(4)	164·3 (2)
N(1)—Ni—N(4)	82·5 (3)	N(3)—Ni—N(4)	93·0 (3)
N(2)—Ni—N(12)	99·0 (3)	N(1)—Ni—N(12)	178·3 (4)
N(3)—Ni—N(12)	97·4 (2)	N(4)—Ni—N(12)	96·0 (3)
N(2)—Ni—N(11)	87·1 (3)	N(1)—Ni—N(11)	98·9 (2)
N(3)—Ni—N(11)	176·7 (3)	N(4)—Ni—N(11)	90·3 (3)
N(12)—Ni—N(11)	81·8 (2)	Ni—N(2)—C(2)	109·5 (6)
N(2)—C(2)—C(1)	109·8 (7)	C(2)—C(1)—N(1)	110·8 (6)
Ni—N(1)—C(1)	106·4 (5)	Ni—N(1)—C(3)	110·4 (4)
C(1)—N(1)—C(3)	110·7 (7)	Ni—N(1)—C(5)	103·9 (4)
C(1)—N(1)—C(5)	111·9 (6)	C(3)—N(1)—C(5)	113·1 (8)
N(1)—C(3)—C(4)	115·1 (6)	C(3)—C(4)—N(3)	113·2 (11)
Ni—N(3)—C(4)	108·9 (4)	N(1)—C(5)—C(6)	110·7 (6)
C(5)—C(6)—N(4)	109·5 (9)	Ni—N(4)—C(6)	109·5 (6)
Ni—N(12)—C(11)	108·3 (3)	Ni—N(12)—C(13)	117·0 (5)
C(11)—N(12)—C(13)	112·3 (6)	Ni—N(11)—C(12)	106·1 (4)
N(11)—C(12)—C(11)	109·7 (9)	N(12)—C(11)—C(12)	109·3 (6)
N(12)—C(13)—C(13′)	114·4 (11)	O(11)—Cl(1)—O(12)	114·5 (5)
O(11)—Cl(1)—O(13)	109·9 (6)	O(12)—Cl(1)—O(13)	109·0 (6)
O(11)—Cl(1)—O(14)	109·6 (4)	O(12)—Cl(1)—O(14)	111·0 (6)
O(13)—Cl(1)—O(14)	102·2 (6)	O(21)—Cl(2)—O(23)	106·1 (10)
O(21)—Cl(2)—O(24)	56·7 (10)	O(23)—Cl(2)—O(24)	57·5 (9)
O(21)—Cl(2)—O(22)	94·6 (6)	O(23)—Cl(2)—O(22)	100·4 (6)
O(24)—Cl(2)—O(22)	127·9 (9)	O(21)—Cl(2)—O(21*a*)	170·7 (11)
O(23)—Cl(2)—O(21*a*)	72·2 (10)	O(24)—Cl(2)—O(21*a*)	116·7 (11)
O(22)—Cl(2)—O(21*a*)	94·6 (6)	O(21)—Cl(2)—O(23*a*)	72·2 (10)
O(23)—Cl(2)—O(23*a*)	159·1 (12)	O(24)—Cl(2)—O(23*a*)	108·4 (9)
O(22)—Cl(2)—O(23*a*)	100·4 (6)	O(21)—Cl(2)—O(24*a*)	116·7 (11)
O(23)—Cl(2)—O(24*a*)	108·4 (9)	O(24)—Cl(2)—O(24*a*)	104·3 (17)
O(22)—Cl(2)—O(24*a*)	127·9 (9)	Cl(2)—O(21)—O(24)	61·4 (14)
Cl(2)—O(21)—O(23*a*)	57·5 (9)	O(24)—O(21)—O(23*a*)	101·1 (18)
Cl(2)—O(23)—O(24)	56·3 (9)	Cl(2)—O(23)—O(21*a*)	50·3 (7)
O(24)—O(23)—O(21*a*)	97·8 (14)	Cl(2)—O(24)—O(21)	61·8 (11)
Cl(2)—O(24)—O(23)	66·2 (13)	O(21)—O(24)—O(23)	117·7 (15)

O(12)···N(11)	3·276	O(32)···N(12)	3·257
O(13)···N(2)	3·124	O(21)···N(3)	3·029
O(13)···N(11)	3·275	O(23)···N(4)	3·230
O(14)···N(4)	3·125	O(24)···N(4)	3·096
O(31)···N(2)	3·240	O(24)···N(4)	3·149
O(31)···N(12)	3·222		

The existence of a bridging arrangement for the trien ligand is quite surprising. Such linkages are clearly entropically unfavorable and consequently occur quite rarely. The occurrence here, in the solid state, may be the consequence of several factors. In addition to ubiquitous crystal-packing forces, the inherent preference for N coordination over O coordination for Ni^{II} complexes leads to NiN_6 rather than an aqua NiN_4O_2 coordination sphere. The increased stability of polydentate ligands as compared to monodentate ligands will dictate a 2:3 metal/ligand ratio. Since the tren ligand is incapable of acting as a bridging bis(bidentate) ligand, the complex will preferentially crystallize in the observed stoichiometry, even if the fraction of trien in solution is smaller than the stoichiometric quantity. Thus, it seems likely that the stable Ni^{II}–tren complex in solution is the *cis*-octahedral $Ni(tren)(H_2O)_2^{2+}$ species.

The perchlorate ions occupy three different sites; Cl(1) is in general positions and the O atoms are ordered; Cl(2) is on a twofold axis with O(22) also on the twofold axis and the other three atoms disordered; Cl(3) is on a twofold axis, but no disorder is present. Thermal amplitudes of vibration are large for all of the O atoms on the perchlorate ions, but except for O(24) do not show any abnormally large amplitudes in any direction. All bond distances are reasonable, 1·36–1·40 Å (uncorrected for riding), again except for Cl(2)—O(24), which is 1·49 Å. Numerous N—H···O contacts exist between the perchlorate anions and the complex ion. Distances range from 3·029 out to approximately 3·3 Å (see Table 2).

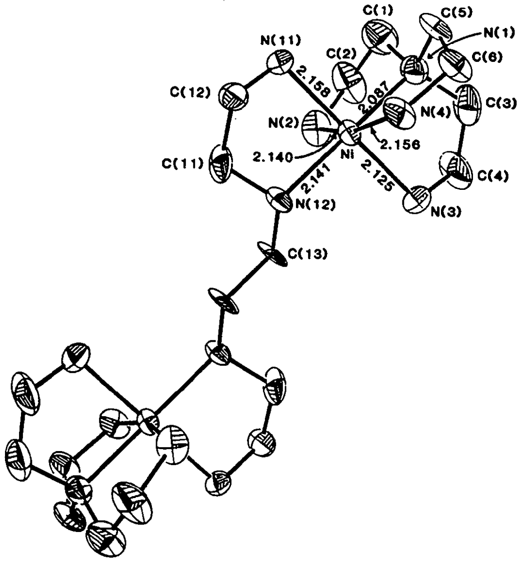

Fig. 1. Illustration of the $[Ni_2(tren)_2trien)]$ dimer in $[Ni_2(tren)_2(trien)](ClO_4)_4$.

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Acta Cryst. (1987). C**43**, 1497–1500

Structure of Catalytically Related Species Involving Copper(II) Halides. III. 2-Amino-5-bromo-3-methylpyridinium 2-Amino-3-methylpyridinium Tetrabromocuprate(II)

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Abstract. $C_6H_8BrN_2^+.C_6H_9N_2^+.CuBr_4^{2-}$, $M_r = 680{\cdot}5$, monoclinic, $P2_1/a$, $a = 15{\cdot}913\ (5)$, $b = 7{\cdot}764\ (3)$, $c = 16{\cdot}297\ (5)$ Å, $\beta = 97{\cdot}33\ (2)°$, $V = 1996{\cdot}9\ (4)$ Å^3, $Z = 4$, $D_x = 2{\cdot}27$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 110{\cdot}1$ cm^{-1}, $F(000) = 1284$, $T = 293$ K, 1719 unique reflections of which 1063 had $F \geq 3\sigma(F)$ were refined to a final $R = 0{\cdot}0593$ for the 3σ data set ($wR = 0{\cdot}0455$). The compound has nominal formula $(C_6H_8BrN_2)(C_6H_9N_2)CuBr_4$ consisting of a 2-amino-5-bromo-3-methylpyridinium cation, a 2-amino-3-methylpyridinium cation and a $CuBr_4^{2-}$ anion. The 5-bromo cations were formed by catalytic bromination of the substituted pyridinium rings by copper(II) bromide. The structure is such that nearly every second cation is the 5-bromo derivative, but this is replaced by the unbrominated cation about 22% of the time, which in turn causes disorder of the $CuBr_4^{2-}$ anion. The $CuBr_4^{2-}$ anion has geometry intermediate between square planar and tetrahedral with Cu—Br (average) 2·376 Å and Br—Cu—Br angles varying between 94·7 (1) and 131·5 (1)°.

Introduction. A series of quasi-planar copper bromide salts analogous to known copper chloride salts has been sought using 2-amino-*n*-methylpyridinium cations (where $n = 3$, 4, 5 or 6) in order to form the $Cu_mX_{2m+2}^{2-}$ cation (where $m = 3$ or 4) or related $Cu_mX_{2m}L_2$ oligomers ($X = Cl^-$ or Br^-). Frequently, crystals containing the $CuBr_4^{2-}$ anion are produced as the only product (Place & Willett, 1987). In the preparation of the 2-amino-3-methylpyridinium copper bromide salts, the only crystalline product turned out to contain the tetrabromide anion, and also had the unusual result of containing partially brominated cations. The catalytic activity of copper(II) halides is known (Hay, Blanchard, Endres & Austance, 1959; Rogic, Demmin & Hammond, 1976). The crystal structures (papers I and II of this series) of the catalytically active species and the phenoxide precursor for the catalytic oxidation of phenols by copper(II) chlorides have been reported (Willett & Breneman, 1983; Marengo-Rullàn & Willett, 1986).

Experimental. An aqueous solution of 1·0 *M* 2-amino-3-methylpyridine was added to a fourfold excess of 1·0 *M* $CuBr_2$ with sufficient 1·0 *M* HBr added to just dissolve any $Cu(OH)_2$ formed. Excess acid was avoided. The solution was warmed for about 3 h. The solution was allowed to evaporate very slowly over several weeks, yielding dark-brown-black plate-like crystals. A crystal approximately 0·1 × 0·15 × 0·05 mm was selected for data collection. Data were collected with an ω scan on a Nicolet *R3m/E* diffractometer system with Mo $K\alpha$ radiation and a graphite monochromator (Campana, Shepherd & Litchman, 1980). Agreement between equivalent reflections was 0·0659. The monoclinic cell and orientation matrix were defined by a least-squares refinement of 25 reflections in the 28–30° 2θ range. The space group was $P2_1/a$ with systematic absences *h*0*l*, *h* odd; 0*k*0, *k* odd. Empirical ψ-scan absorption corrections were applied assuming an ellipsoidal shaped crystal (min. transmission 0·193, max. transmission 0·347). Data were collected for $h \geq 0$, $k \geq 0$ and all *l*. (The max. values

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