tilted 21·6 (1)° around an axis parallel to [010]. Between these rows lie rows of Sr2—O_8 square prisms linked with two vertices to each other and with two vertices to two Sb1—O_6 octahedra, forming slabs perpendicular to [010]. This part of the structure is basically the same as parts of the structure of La_3NbO_7 (Rossell, 1979) and pyrochlore. The difference is in the arrangement of the ions between these slabs as was described by Rossell (1979). The Sb2—O_6 octahedra lie between the above-mentioned slabs and share four corners with Sb1—O_6 octahedra and two corners with Sr2—O_8 square prisms. The Sr1—O_8 hexagonal prisms share four vertices with Sb1—O_6 octahedra and two vertices parallel to (100) with the Sb2—O_6 octahedra (Fig. 2). The difference from the pyrochlore structure can be described as follows. In the pyrochlore structure all large cations have a cubic 8 coordination. In the weberite structure these ions occur in one square and one hexagonal biprism. The way the octahedra are connected is also different. In the pyrochlore structure all the octahedra are connected to six identical octahedra. In the weberite structure one type (Sb1) is connected to six octahedra, the other (Sb2) is connected to four octahedra.

The weberite structure does not exist for M^{5+} = Nb and Ta but it does exist for the larger U^{5+} ion (Cordfunke & IJdo, 1988).

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Synthesis and Structure of Pentaamminephosphatocobalt(III)–Silver Nitrate–Water (1/3/1) (I) and Pentaamminephosphatocobalt(III)–Water (1/2) (II)

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Abstract. (I) $[CoPO_4(NH_3)_5].3AgNO_3.H_2O$, M_r = 766·70, monoclinic, $P2_1/c$, $a = 6·800$ (1), b = 9·344 (1), c = 27·087 (3) Å, $\beta = 93·66$ (1)°, V = 1717·4 (3) Å^3, $Z = 4$, $D_m = 2·87$, $D_x = 2·965$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 44·4$ cm^{-1}, $F(000)$ = 1472, $T = 296$ (2) K. (II) $[CoPO_4(NH_3)_5].2H_2O$, M_r = 275·08, monoclinic, $P2_1/c$, $a = 6·401$ (1), b = 11·048 (1), $c = 13·839$ (2) Å, $\beta = 104·55$ (1)°, V = 947·2 (2) Å^3, $Z = 4$, $D_m = 1·91$, $D_x = 1·930$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 20·7$ cm^{-1}, $F(000) = 576$, $T = 296$ (2) K. Final R values 0·0282 (I) and 0·0209 (II) for 2075 and 1425 observed reflections with $F_o \geq 6·0\sigma(F_o)$. Co is hexacoordinate in both structures with an octahedral geometry. Two of the three independent Ag atoms have 2+2 coordination and form centrosymmetric dimers with an $(AgO_2P)_2$ core, while the third Ag atom is pentacoordinate with a distorted tetragonal pyramidal geometry.

Introduction. Metal ions coordinated to the phosphate groups of nucleotides promote, in living cells, phosphate ester hydrolysis and maintain polynucleotide structure (Spiro, 1980). The complex between Mg^{2+} and ATP is a necessary cofactor for phosphoryl and nucleotidyl transfer enzymes. There are several examples of structurally known metal-ion nucleotide complexes, such as Co^{2+}, Zn^{2+}, Hg^{2+}, Cu^{2+}, Cd^{2+}, Pt^{2+} strongly bonded to the phosphate group (Spiro, 1980),

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Table 1. *Positional and equivalent isotropic thermal parameters* ($\times 10^4$) *of the non-hydrogen atoms with e.s.d.'s of the positional parameters in parentheses*

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

	x	y	z	U_{eq}(Å^2)
(I)				
Co	-4133 (1)	7967·3 (7)	3625·8 (2)	206
P	-220 (2)	7466 (1)	4320·6 (5)	193
N(1)	-4888 (6)	8519 (6)	4281 (2)	356
N(2)	-6587 (7)	8757 (5)	3335 (2)	317
N(3)	-2775 (7)	9783 (5)	3562 (2)	321
N(4)	-5439 (7)	6151 (5)	3695 (2)	293
N(5)	-3367 (7)	7422 (5)	2970 (2)	296
O(1)	1276 (5)	2478 (4)	5189 (1)	253
O(2)	1399 (5)	6331 (4)	4342 (1)	307
O(3)	656 (5)	8919 (4)	4208 (1)	259
O(4)	-1763 (5)	7025 (3)	3899 (1)	215
Ag(1)	1942·1 (8)	4465·2 (5)	4804·8 (2)	438
Ag(2)	-724·7 (8)	4489·0 (5)	3796·0 (2)	488
Ag(3)	833·1 (8)	898·2 (5)	4610·1 (2)	432
N(6)	1318 (8)	5574 (6)	2635 (2)	455
N(7)	6177 (8)	2770 (5)	4467 (2)	388
N(8)	2535 (8)	2396 (5)	3475 (2)	450
O(61)	276 (8)	4625 (6)	2431 (2)	798
O(62)	3003 (7)	5800 (6)	2491 (2)	638
O(63)	732 (6)	6255 (5)	2989 (2)	531
O(71)	-2305 (7)	2565 (5)	4247 (2)	583
O(72)	5646 (7)	3997 (5)	4567 (2)	593
O(73)	-4820 (10)	1740 (6)	4578 (3)	986
O(81)	1300 (10)	1578 (8)	3615 (4)	1003
O(82)	3942 (9)	1905 (7)	3224 (2)	501
O(83)	2400 (10)	3618 (7)	3563 (4)	818
O(84)	1680 (30)	2660 (20)	3882 (9)	1033
O(85)	1920 (30)	3310 (20)	3200 (10)	1230
O(86)	4080 (30)	1930 (20)	3470 (10)	1231
O(*W*)	-2950 (8)	4024 (5)	3062 (2)	615
(II)				
Co	588·4 (4)	1933·8 (2)	3739·6 (2)	134
P	-3240·0 (8)	109·9 (5)	2857·6 (4)	147
N(1)	3499 (3)	2616 (2)	3998 (1)	201
N(2)	-691 (3)	3467 (2)	3203 (1)	202
N(3)	1882 (3)	404 (2)	4304 (1)	198
N(4)	934 (3)	1501 (2)	2416 (1)	192
N(5)	258 (3)	2463 (2)	5043 (1)	204
O(1)	-5464 (2)	−141 (2)	3029 (1)	298
O(2)	−1724 (2)	−962 (1)	3229 (1)	225
O(3)	-3394 (2)	321 (2)	1739 (1)	235
O(4)	-2318 (2)	1269 (1)	3466 (1)	191
O(*W*1)	-7403 (3)	23 (2)	338 (1)	362
O(*W*2)	-4027 (3)	2671 (2)	1032 (1)	365

as well as the N atoms of the base residue of the nucleotides.

We report here the synthesis and structure of $Co(NH_3)_5PO_4$ (II) and $Co(NH_3)PO_4.3AgNO_3$ (I). In the latter complex the silver ions are bonded to the Co-coordinated phosphate group. This structure would provide a simple example of the silver ion bonding to the phosphate group, similar to that of Mg^{2+} phosphate binding in ATP.

Some features of (I) were presented at the IX European Crystallographic Meeting (Terzis & Mentzafos, 1985).

Experimental. (II) was synthesized by routine methods (Schmidt & Taube, 1963). (I) was prepared by addition of $AgNO_3$ and $Co(NH_3)_5PO_4$ in water in 3:1 mole ratio and crystallized by slow evaporation of the solution at room temperature. D_m measured by flotation. Crystal dimensions 0·40 × 0·09 × 0·09 (I) and 0·25 × 0·20 × 0·20 mm (II). Syntex $P2_1$ diffractometer. θ–2θ scan, $2\theta \leq 48{\cdot}0$ (I) and 49·0° (II), scan speed variable between 1·0° and 8·0° min^{-1}, scan range 1·6° (2θ) plus α_1–α_2 separation, background counting 0·4 (I) and 0·5 (II) of scan time. Cell parameters from 15 independent reflections with $19 < 2\theta < 23°$ (I) and $15 < 2\theta < 26°$ (II). Data collected/observed $[F \geq 6{\cdot}0\sigma(F)]/R_{\rm int}(F)$, 3160/2709/0·0257 (I) and 3290/1582/0·0161 (II). Range of hkl: 0→7, 0→10, −31→31 (I) and −7→7, 0→12, −16→16 (II). Three reflections monitored periodically showed < 3·0% intensity fluctuation. Lp and empirical φ-scan absorption correction applied (Syntex, 1976).

The Ag-atom positions in (I) deduced from an E map. The Co-atom position in (II) from a Patterson synthesis. In both cases subsequent difference Fourier synthesis revealed the positions of all the other non-H atoms. Refinement, based on F, by full-matrix least squares minimizing $\sum w\Delta^2$ with *SHELX*76 (Sheldrick, 1976). H atoms located from ΔF maps. Non-H atoms anisotropic, H atoms isotropic (coordinates refined). Weighting scheme for the last steps of refinement $1/w = \sigma^2(F_o) + g|F_o|^2$, $g = 0{\cdot}00034$ (I) and 0·00020 (II). Number of refined parameters 340 (I) and 194 (II). $S = 1{\cdot}53$ (I) and 2·50 (II) for observed reflections. Seven reflections in (I), showing strong extinction effects, were given zero weight during final refinement cycles. $wR = 0{\cdot}0325$ (I) and 0·0282 (II) for observed data. $R/wR = 0{\cdot}0433/0{\cdot}0372$ (I) and 0·0244/0·0294 (II) for all data. $\Delta\rho_{\rm max}/\Delta\rho_{\rm min} = 0{\cdot}567/-0{\cdot}863$ (I) and 0·364/0·235 e Å^{-3} (II). $|\Delta/\sigma|_{\rm max} = 0{\cdot}053$ (I) and 0·091 (II). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic parameters of the non-H atoms are given in Table 1.*

One of the nitrate groups is disordered. We included two models in the refinement and their site occupancies were refined keeping the sum of the two constant at 1. They refined to 0·75 for O(81), O(82) and O(83). Still the bond distances and angles for the disordered nitrate were not satisfactory. They varied between 1·14 (2) and 1·30 (2) Å and 103 (1) and 124 (1)° respectively, while for the other nitrate groups the variation was between 1·225 (8) and 1·243 (9) Å and 119·2 (5) and 120·8 (5)°.

Discussion. *The* Co *and* P *coordination.* Fig. 1 shows the $Co(NH_3)_5PO_4$ moiety as it appears in both structures and Table 2 contains the bond lengths and angles for this complex. Co has octahedral coordination and P tetrahedral. The dispersion in P—O

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* Lists of observed and calculated structure factors, anisotropic thermal parameters of the non-H atoms and atomic and isotropic thermal parameters of the H-atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44667 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

distances that is observed in both structures [1·521 (4) to 1·557 (3) Å in (I) and 1·526 (2) to 1·565 (1) Å in (II)] is primarily due to the phosphate coordination to Co and Ag in (I) and to its coordination to Co and participation in strong hydrogen bonds in (II). In both structures the longest P—O bond (Table 2) is to O(4) through which the phosphate coordinates to Co. The next longest in (I) is to O(1) through which it coordinates strongly to both Ag(1) and Ag(3), while O(2) and O(3) coordinate strongly to only one Ag ion each, and form the strongest P—O bonds in (I). In (II) the next longest P—O bond is to O(3), which is involved in the strongest hydrogen bond in these structures (Table 3), O(*W*2)···O(3) being 2·769 (2) Å and O(*W*2)—H(22)—O(3) 159 (1)°.

Coordination of Ag. Fig. 2 shows the coordination of the silver atoms. It is accepted that Ag···O contacts shorter than 3·0 Å denote an interaction between them (Gagnon & Beauchamp, 1977). For Ag—O distances of about 2·1 Å the interaction is accepted as a covalent bond since the sum of the covalent radii for Ag and O atoms is about 2·1 Å (Pauling, 1960) and since such short Ag—O distances are observed only with an approximately linear O—Ag—O coordination. For Ag—O distances of about 2·5 Å the interaction is accepted as mainly ionic, since such lengths are found in compounds such as $AgClO_3$, $AgClO_4$, $KAgCO_3$, $AgClO_2$, $AgNO_2$ (Fleming & Lynton, 1968). There are also many reports of Ag—O contacts in the range of

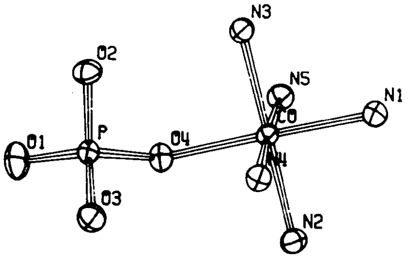


Fig. 1. A view of the $Co(NH_3)_5PO_4$ moiety, drawn with the coordinates of (II). The N labels in the two structures are related by cyclic permutations: N(1,2,3,4,5) in (II) correspond to N(2,3,4,5,1) in (I). The other labels are the same.

Table 2. *Bond lengths* (Å) *and angles* (°) *of the* $Co(NH_3)_5PO_4$ *moiety with e.s.d.'s in parentheses*

	(I)	(II)		(I)	(II)
Co—N(1)	1·949 (5)	1·958 (2)	Co—O(4)	1·941 (3)	1·947 (1)
Co—N(2)	1·945 (4)	1·946 (2)	P—O(1)	1·551 (2)	1·526 (2)
Co—N(3)	1·944 (5)	1·957 (2)	P—O(2)	1·528 (4)	1·535 (2)
Co—N(4)	1·930 (5)	1·958 (2)	P—O(3)	1·521 (4)	1·544 (2)
Co—N(5)	1·950 (5)	1·957 (2)	P—O(4)	1·557 (3)	1·565 (1)
N(1)—Co—N(2)	90·0 (2)	91·4 (1)	N(3)—Co—O(4)	92·4 (2)	92·3 (1)
N(1)—Co—N(3)	90·3 (2)	88·4 (1)	N(4)—Co—N(5)	90·6 (2)	176·7 (1)
N(1)—Co—N(4)	89·7 (2)	86·5 (1)	N(4)—Co—O(4)	86·6 (2)	93·0 (1)
N(1)—Co—N(5)	179·7 (1)	92·0 (1)	N(5)—Co—O(4)	88·0 (2)	88·4 (1)
N(1)—Co—O(4)	91·9 (2)	179·2 (1)	O(1)—P—O(2)	111·3 (2)	110·1 (1)
N(2)—Co—N(3)	91·9 (2)	179·0 (1)	O(1)—P—O(3)	110·5 (2)	110·9 (1)
N(2)—Co—N(4)	89·2 (2)	89·5 (1)	O(1)—P—O(4)	108·1 (2)	107·8 (1)
N(2)—Co—N(5)	90·1 (2)	87·7 (1)	O(2)—P—O(3)	109·7 (2)	109·1 (1)
N(2)—Co—O(4)	175·3 (2)	87·9 (1)	O(2)—P—O(4)	107·1 (2)	109·3 (1)
N(3)—Co—N(4)	179·0 (2)	91·5 (1)	O(3)—P—O(4)	110·1 (2)	109·6 (1)
N(3)—Co—N(5)	89·5 (2)	91·3 (1)	P—O(4)—Co	131·6 (2)	128·8 (1)

Table 3. *X···Y and* Ag···Ag *distances across the eight-membered ring*

	XYZ group	*X···Y* (Å)	Ag···Ag (Å)
1	O—C—O in glycylglycine	2·243	2·924
2	O—C—O in glycine	2·244	2·877
3	O—C—O in trifluoroacetate	2·242	2·893
4	N(3)—C(2)—O(2) in cytosine	2·280	3·370
5	N(3)—O(4)—N(9) in adenine	2·425	3·002
6	O—P—O present	2·54 (2)	3·075 (1)
7	O—P—O present	2·52 (2)	2·979 (1)
8	P—C—P in dpm	3·040	3·085

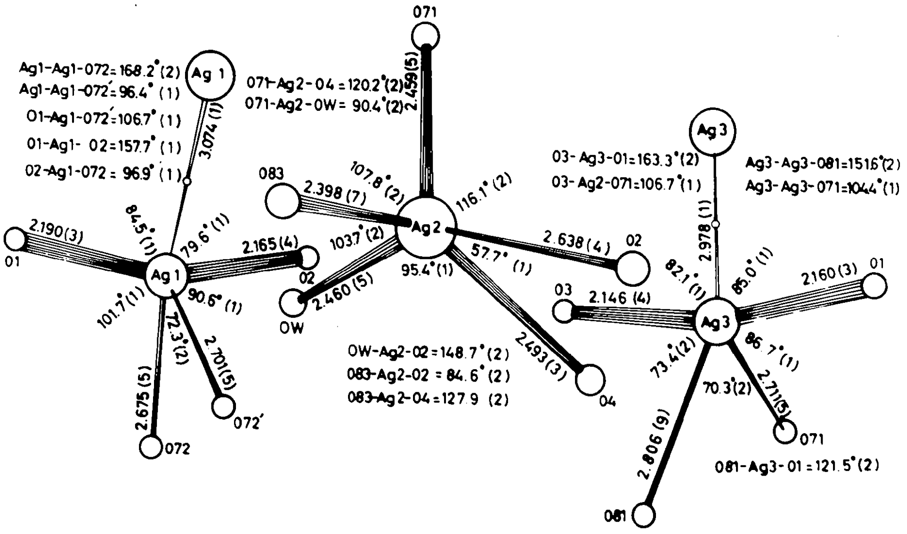


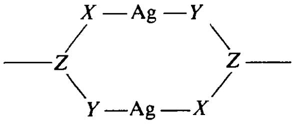
Fig. 2. The coordination of the silver atoms.

2·7–3·0 Å (Ho & Bau, 1983; Fleming & Lynton, 1968). In this investigation we observe interactions of all three types.

Ag(1) and Ag(3) each form two strong covalent bonds to phosphate O atoms at O—Ag—O angles of 157·7 and 163·3° respectively. They also have two weak interactions each, 2·674 to 2·800 Å, with nitrate oxygens. This type of silver coordination, formed by two short bonds in an almost linear arrangement, with one to four additional weaker interactions, which we can call 2+1 through 2+4 coordination, is quite frequent [Fleming & Lynton, 1968 (2+2); Gagnon & Beauchamp, 1977 (2+1 and 2+3); Gagnon, Hubert, Rivest & Beauchamp, 1977 (2+3); Ho & Bau, 1983 (2+2 and 2+1); Mak, 1984 (2+4)]. In our case the coordination is 2+2.

The third silver atom, Ag(2), surrounded by five oxygens has the coordination of a distorted tetragonal pyramid (Mak, 1984). Four Ag(2)—O distances in the range of 2·4–2·5 Å are mainly ionic interactions. The fifth, Ag(2)—O(2) is significantly longer. O(2) is already strongly coordinated to Ag(1).

Ag(1) and Ag(2) form centrosymmetric dimers with $Ag_2O_4P_2$ cores having the chair conformation. Adjacent dimers share a P—O bond and form extensive chains parallel to the *b* axis at $c \simeq 0$ and $c \simeq 0{\cdot}5$. A view of the molecular packing is given in Fig. 3. In Ag^+ chemistry it is rather common to observe the formation of flexible eight-membered rings, either planar (Acland & Freeman, 1971), or with a boat conformation (Ho & Bau, 1983), or a chair conformation (Kistenmacher, Rossi & Marzilli, 1979) as in our case. In the formation of these eight-membered rings the bite *XYZ* and the type of coordinating atoms *X,Y* seem to play a determining role, but because of the flexibility of the Ag^+ coordination there is no shortage of ligands that form the eight-membered ring. The *YZX* part can be the carboxyl group (Acland & Freeman, 1971; Hunt, Lee & Amma, 1974; Rao & Viswamitra, 1972), the N(3)—C(2)—O(2) moiety of the cytosine ligand (Kistenmacher, Rossi & Marzilli, 1979), the N(9)—C(4)—N(3) moiety of adenine (Gagnon, Hubert, Rivest & Beauchamp, 1977), the P—C—P part of bis(diphenylphosphino)methane (dpm) (Ho & Bau, 1983), or in the present case the phosphate group.



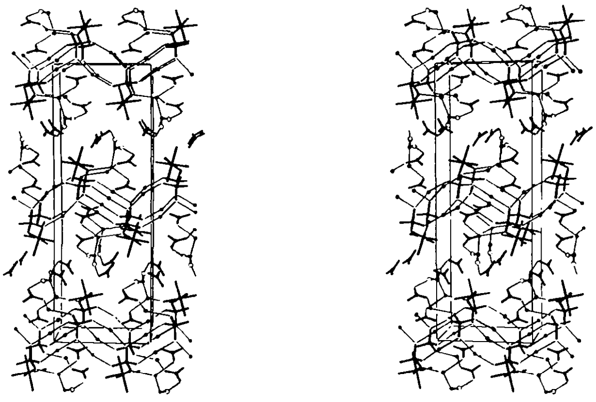


Fig. 3. A stereoview of the molecular packing of (I) looking down the *a* axis.

Table 4. *Donor–acceptor distances* (Å) *and angles* (°) *around the* H *atoms in the hydrogen bonds*

D—H···*A*	*D*···*A*	*D*—H···*A*
(I)		
N(1)—H(1*A*)···O(3)	3·047 (5)	150 (2)
N(1)—H(1*B*)···O(1)	2·917 (6)	155 (2)
N(2)—H(2*C*)···O(63)	3·074 (7)	156 (3)
N(3)—H(3*B*)···O(3)	2·939 (6)	145 (3)
N(3)—H(3*C*)···O(62)	3·000 (7)	170 (3)
N(4)—H(4*C*)···O(2)	2·864 (6)	140 (3)
N(5)—H(5*C*)···O(63)	2·990 (6)	169 (2)
O(*W*)—H(*WA*)···O(61)	2·920 (8)	149 (3)
O(*W*)—H(*WB*)···O(82)	2·950 (8)	153 (2)
(II)		
N(1)—H(1*A*)···O(*W*2)	2·879 (2)	163 (1)
N(2)—H(2*B*)···O(2)	2·872 (3)	163 (1)
N(3)—H(3*A*)···O(2)	2·844 (2)	156 (1)
N(3)—H(3*C*)···O(1)	2·806 (3)	162 (1)
N(4)—H(4*A*)···O(1)	2·889 (2)	159·1 (8)
N(4)—H(4*B*)···O(2)	3·022 (2)	164 (1)
N(4)—H(4*C*)···O(3)	2·991 (2)	152·3 (8)
N(5)—H(5*C*)···O(2)	2·868 (2)	167 (1)
O(*W*1)—H(11)···O(3)	2·820 (2)	172 (1)
O(*W*1)—H(12)···O(3)	3·067 (2)	168 (2)
O(*W*2)—H(21)···O(1)	2·802 (3)	158 (1)
O(*W*2)—H(22)···O(3)	2·769 (2)	159 (1)

Table 3 compares the 'bite' of the various ligands, as indicated by the distance *X*···*Y*, and the Ag···Ag distance across the eight-membered ring. If for the moment we leave out example 4, we see that while the 'bite' spans 0·8 Å the Ag···Ag separations stay relatively constant and there is no correlation between 'bite' and Ag···Ag distance. This is particularly emphasized if we compare example 6 with example 8; for a 0·5 Å increase in bite there is only a 0·01 Å increase in Ag···Ag distance. Kistenmacher *et al.* (1979), in comparing 4 with 1, 2 and 3, suggested that the anomalously large Ag···Ag distance in example 4 may be due to the smaller ability of cytosine to delocalize the positive charge of Ag^+ and the consequently large Coulombic repulsion between the Ag^+ ions. This suggestion remains valid in view of structures 5,6,7 and 8. All the ligands are either anionic or have large π systems which can delocalize the positive charge of the Ag^+. In view of this and the fact that the Ag···Ag distances in all complexes but number 4 are close to the Ag···Ag separations in Ag metal, 2·89 Å (Kistenmacher *et al.*, 1979), the question of metal–metal bonding poses itself again. It is not an easy question to settle (Jennische & Hesse, 1971) and authors have considered such separations as nonbonding and determined primarily by the ligand bite (Gagnon, Hubert, Rivest & Beauchamp, 1977; Hunt, Lee & Amma, 1974). But if the ligand can delocalize the positive charge of $\mathrm{Ag^+}$, in which case the Ag···Ag separation is observed to be independent of ligand bite and stays relatively constant close to the Ag···Ag separation in Ag metal, metal–metal bonding cannot be ruled out.

Hydrogen bonds. There are hydrogen bonds in both structures and they are listed in Table 4. We have accepted as such only the cases with N···O and O···O distances shorter than 3·1 and 3·0 Å and *D*—H···*A* angle greater than 140°.

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Structure de $\mathrm{Na_2As_4O_{11}}$

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Abstract. Disodium tetraarsenate, $M_r = 521{\cdot}66$, monoclinic, $C2/c$, $a = 9{\cdot}049$ (3), $b = 8{\cdot}287$ (3), $c = 11{\cdot}508$ (5) Å, $\beta = 102{\cdot}74$ (4)°, $V = 842$ (2) Å^3, $Z = 4$, $D_m = 4{\cdot}06$ (by flotation), $D_x = 4{\cdot}11$ Mg m^{-3}, $\lambda(\mathrm{Ag}\ K\overline{\alpha}) = 0{\cdot}5608$ Å, $\mu = 8{\cdot}6$ mm^{-1}, $F(000) = 968$, room temperature, final $R = 0{\cdot}046$ and $wR = 0{\cdot}048$ for 1153 independent reflections. The main feature of this structure is the existence of the first three-dimensional anion $(\mathrm{As_4O_{11}})_n^{2n-}$ in the chemistry of the condensed arsenates. It has the lowest O/As ratio (2·75) of the known arsenates showing marked condensation: all the O atoms are shared except one per $\mathrm{AsO_4}$ tetrahedron. The structural unit is the $\mathrm{As_4O_{15}}$ ring with point symmetry 2, built up from alternate $\mathrm{AsO_4}$ tetrahedra and $\mathrm{AsO_6}$ octahedra sharing corners. In addition, the two octahedra share one O atom located on the 2 axis. The $\mathrm{As_4O_{15}}$ ring derives from the known centrosymmetric $\mathrm{As_4O_{14}}$ ring by the cleavage of one As—O—As linkage between the two octahedra of the ring to form two new As—O—As linkages with $\mathrm{AsO_4}$ tetrahedra connecting two rings, leading to a decrease of the O/As ratio. The $\mathrm{As_4O_{15}}$ rings are further linked by sharing edges of $\mathrm{AsO_6}$ octahedra to form a three-dimensional framework. This completes the set of the already known arrangements of the $\mathrm{As_4O_{14}}$ ring (isolated units, infinite chains, layers).

Introduction. Dans le cadre de l'étude entreprise sur les arséniates condensés nous avons constaté que le rapport O/As le plus bas pour les sels connus est égal à trois par exemple pour $\mathrm{NaHAs_2O_6}$ (Nguyen-Huy Dung & Jouini, 1978) et $\mathrm{NaH_2As_3O_9}$ (Driss, Averbuch-Pouchot, Durif & Jouini, 1988). Nous avons cherché à diminuer ce rapport, autrement dit à augmenter le nombre de liaisons entre polyèdres $\mathrm{AsO_4}$ et/ou $\mathrm{AsO_6}$ en éliminant la présence d'eau des mélanges par le travail dans la zone acide ($\mathrm{Na_2O/As_2O_5} < 1$) du système binaire $\mathrm{Na_2O}$—$\mathrm{As_2O_5}$. L'étude de ce système (Amadori, 1914)

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