Discussion. The structure is isomorphous with other Na pyroxenes (Clark *et al.*, 1969). Mn occupies a strongly distorted octahedral ($M1$) site. The distortion shows that there exists Jahn–Teller stabilization of Mn^{3+} in this pyroxene structure. Table 3 summarizes the $M1-M1$ and the mean $M1-O1$ distances and the $M1-O1-M1$ angles in the series of Na pyroxenes. The $M1-M1$ distance is nearly the same as twice the product of the mean $M1-O1$ distance and the sine of one-half of the $M1-O1-M1$ angle as listed in the second and fifth columns of Table 3. The variation of the $M1-M1$ distance across the shared O1–O1 edge with the mean $M1-O1$ distance is shown in Fig. 1 (lower curve); a smooth curve can be drawn through those points representing the Al, Ga, Fe, Sc, and In members but the Ti, V, Cr and Mn members deviate from the trend. The $M1-M1$ distances in the latter are shorter than those estimated from the mean $M1-O1$ distances. The shorter $M1-M1$ distances correlate with the smaller $M1-O1-M1$ angles as shown in Fig. 1 (upper curve). Hawthorne & Grundy (1973) predicted that the short metal–metal distance in $CrNaSi_2O_6$ and the suspected anomalous metal–metal distances in $TiNaSi_2O_6$ and $VNaSi_2O_6$ should be due to metal–metal bonds. However, these metal–metal distances are much longer than the distances in Ti_2O_3 and V_2O_3 with metal–metal bonding (Prewitt, Shannon, Rogers & Sleight, 1969). The shorter $M1-M1$ distances in pyroxenes may be caused by the geometrical features of the $M1$ sites. The sum of the $M1-O1-M1$ and the $O1A1-M1-O1B2$ angles is $180°$. Therefore, the smaller $M1-O1-M1$ angles correspond to the larger $O1A1-M1-O1B2$ angles. The larger $O1A1-M1-O1B2$ angles may be caused by the repulsions between the O1 atoms and the non-bonding $3d$ electrons of the Ti, V, Cr and Mn ions. That is, the shorter metal–metal approaches may be correlated with the geometry of the $M1O_6$ octahedron.

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Trichloroselenonium(IV) Tetrachloroaurate(III)

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Abstract. $[SeCl_3][AuCl_4]$, $M_r = 524·1$, monoclinic, $P2_1/c$, $a = 8·484$ (3), $b = 10·184$ (3), $c = 12·135$ (4) Å, $\beta = 108·37$ (3)°, $V = 995·1$ Å^3, $Z = 4$, $D_x = 3·50$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0·71069$ Å, $\mu = 20·2$ mm^{-1}, $F(000) = 928$, $T = 293$ K, $R = 0·069$, $wR = 0·059$ for 1139 reflections. The structure consists of centrosymmetric $[SeCl_3.AuCl_4]_2$ dimers; the coordination geometry at selenium (including secondary interactions) is distorted octahedral with mean Se–Cl 2·121, Se···Cl 2·941 Å. The compound is not isostructural with its tellurium analogue.

Introduction. Salts that contain the pyramidal cations MX_3^+ (X = halogen; M = S, Se, Te) display charac- teristic secondary interactions between the atom M and the accompanying anions; this generally leads to an extended coordination geometry with a distorted octahedron around M (Christian, Collins, Gillespie & Sawyer, 1986, and references cited therein). Only one such structure involving a square-planar anion had been reported until recently ($SCl_3^+.ICl_4^-$; Edwards, 1978) and we have therefore begun to investigate the structures of $MCl_3^+.AuCl_4^-$. The tellurium derivative (Jones, Jentsch & Schwarzmann, 1986) consists of centrosymmetric dimers in which the extended coordination at tellurium is distorted square pyramidal. Powder data (Novitskaya, Timoshchenko & Fokina, 1979) indicate that the compounds $MCl_3^+.AuCl_4^-$ are not isostructural.

Experimental. The title compound was prepared using a slightly modified version of the method of Lindet (1887) and recrystallized from $AsCl_3$. All compounds involved are very sensitive to atmospheric moisture and appropriate precautions were taken.

Orange crystal, shape approximately cubic, $0.2 \times 0.2 \times 0.2$ mm. Stoe–Siemens four-circle diffractometer, monochromated Mo $K\alpha$ radiation, profile-fitting mode (Clegg, 1981). Three check reflections, no systematic intensity variation. 2322 reflections, $2\theta_{max}$ 50°, quadrant $-h+k\pm l$ and some $+h$ equivalents. Empirical absorption correction based on ψ scans; transmissions 0.56–0.99. 1745 unique reflections (R_{int} 0.047), 1139 with $F > 4\sigma(F)$ used for all calculations (program system SHELXTL; Sheldrick, 1983). Index range: $|h| \le 9$, $|k| \le 12$, $|l| \le 14$. Cell constants refined from 2θ values of 42 reflections in the range 20–23°.

Structure solution by interpretation of Patterson function. Anisotropic refinement on F to $R = 0.069$, $wR = 0.059$. Extinction correction of the form $F_{corr} = F_{calc}/[1 + xF^2/\sin 2\theta]^{0.25}$ with $x = 1.5\,(2) \times 10^{-6}$. Weighting scheme $w^{-1} = \sigma^2(F) + 0.00035F^2$. 83 parameters, $S = 1.37$, max. $\Delta/\sigma = 0.007$, max. features in final $\Delta\rho$ map ± 2 e Å^{-3}. Atomic scattering factors as incorporated in SHELXTL.

Discussion. Final atomic coordinates are presented in Table 1, with associated bond lengths and angles in Table 2.*

The structure consists of centrosymmetric $[SeCl_3.AuCl_4]_2$ dimers (Fig. 1) with mean Se–Cl 2.121, Se···Cl 2.941 Å, Cl–Se–Cl 98.0° (cf. $SeCl_3^+.SbCl_6^-$ 2.095, 3.13 Å, 103° respectively; Christian et al., 1986). The primary coordination geometry at selenium is pyramidal; the secondary interactions complete the usual distorted octahedral geometry. The Au–Cl(4) bond is significantly shorter than the other Au–Cl bonds [2.266 vs 2.295 (av.) Å], reflecting the fact that Cl(4) is not involved in secondary interactions. The shortest Au···Cl contact is 3.48 (1) Å for Cl(7) at $1-x$, $1-y$, $1-z$. Fig. 2 shows the molecular packing.

$SeCl_3^+.AuCl_4^-$ is not isostructural with its $TeCl_3^+$ analogue or with $SCl_3^+.ICl_4^-$.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å$^2 \times 10^3$)

	x	y	z	U_{eq}*
Au	2221 (1)	5835 (1)	5479 (1)	31 (1)
Cl(1)	3829 (10)	4195 (7)	6557 (5)	51 (3)
Cl(2)	1699 (10)	4615 (7)	3806 (5)	51 (3)
Cl(3)	655 (9)	7501 (7)	4399 (6)	47 (3)
Cl(4)	2744 (11)	7070 (7)	7108 (6)	57 (3)
Se	2395 (3)	2044 (2)	4966 (2)	31 (1)
Cl(5)	1055 (10)	915 (7)	3515 (6)	60 (3)
Cl(6)	2868 (10)	577 (7)	6276 (6)	58 (3)
Cl(7)	4722 (10)	1953 (8)	4650 (7)	63 (3)

* Equivalent isotropic U calculated from anisotropic U.

Table 2. *Bond lengths* (Å) *and angles* (°)

|			
Au–Cl(1)	2.289 (7)	Au–Cl(2)	2.301 (7)
Au–Cl(3)	2.294 (8)	Au–Cl(4)	2.266 (8)
Cl(1)···Se	2.920 (8)	Cl(2)···Se	2.944 (8)
Se···Cl(3^i)	2.960 (10)	Cl(5)–Se	2.110 (8)
Cl(6)–Se	2.125 (9)	Cl(7)–Se	2.129 (11)
Cl(1)–Au–Cl(2)	91.4 (3)	Cl(1)–Au–Cl(3)	178.9 (4)
Cl(2)–Au–Cl(3)	88.8 (3)	Cl(1)–Au–Cl(4)	89.4 (3)
Cl(2)–Au–Cl(4)	178.9 (4)	Cl(3)–Au–Cl(4)	90.4 (3)
Cl(1)···Se–Cl(5)	164.4 (4)	Cl(2)···Se–Cl(5)	96.4 (3)
Cl(1)···Se–Cl(6)	95.3 (3)	Cl(2)···Se–Cl(6)	160.9 (4)
Cl(5)–Se–Cl(6)	99.6 (4)	Cl(1)···Se–Cl(7)	86.3 (4)
Cl(2)···Se–Cl(7)	90.6 (4)	Cl(5)–Se–Cl(7)	96.4 (4)
Cl(6)–Se–Cl(7)	97.9 (4)	Cl(1)···Se···Cl(3^i)	85.8 (3)
Cl(2)···Se···Cl(3^i)	85.7 (3)	Cl(5)–Se···Cl(3^i)	91.0 (4)
Cl(6)–Se···Cl(3^i)	83.7 (4)	Cl(7)–Se···Cl(3^i)	172.0 (4)
Cl(1)···Se···Cl(2)	68.1 (3)		

Symmetry code: (i) $-x$, $1-y$, $1-z$.
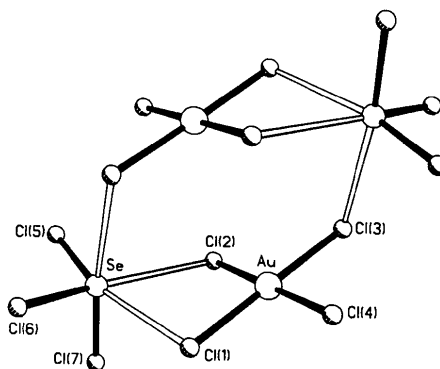
Fig. 1. The centrosymmetric dimer $[SeCl_3.AuCl_4]_2$, showing the atom-numbering scheme. Open bonds indicate secondary Se···Cl contacts.
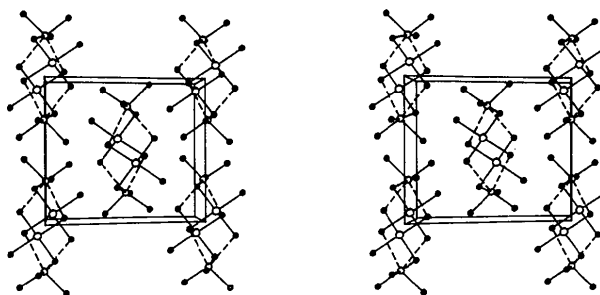

Fig. 2. Stereographic packing diagram of the structure viewed along the z axis: Cl atoms filled; dashed lines indicate secondary interactions.

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Structure du Bis(*cyclo*-triphosphate) de Tétraammonium et de Cobalt(II) Tétrahydraté

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Abstract. $Co(NH_4)_4(P_3O_9)_2.4H_2O$, $M_r = 676.98$, monoclinic, $P2_1/c$, $a = 8.612$ (2), $b = 14.698$ (3), $c = 8.809$ (2) Å, $\beta = 95.67$ (1)°, $V = 1110$ (7) Å^3, $Z = 2$, $D_m = 2.00$ (5), $D_x = 2.03$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0.7107$ Å, $\mu = 1.2981$ mm^{-1}, $F(000) = 690$, $T = 293$ K, final $R = 0.053$ for 1450 observed independent reflexions with $I > 3\sigma(I)$. The structure is a three-dimensional framework based on $[Co(P_3O_9)_2(H_2O)_4]^{4-}$ complex anions linked together by NH_4^+ cations. Co^{2+} is coordinated by four water molecules and two $P_3O_9^{3-}$ ring anions in *trans* positions. The ammonium polyhedra $NH_4(1)O_8$ and $NH_4(2)O_7$ are respectively connected to the CoO_6 octahedron by the $O(W1)$–$O(E12)$ edge and the $O(W2)$ water molecule.

Introduction. L'étude bibliographique des *cyclo*-triphosphates mixtes de cobalt(II) et des monovalents révèle que seuls quelques composés anhydres ont été étudiés (Durif, 1969). Les seul *cyclo*-triphosphate de cobalt hydraté ayant fait l'objet d'une étude structurale est le $CoK_4(P_3O_9)_2.7H_2O$ (Seethanen, Tordjman & Averbuch-Pouchot, 1978). Une étude systématique des hydrates de *cyclo*-triphosphates de cobalt(II) et de monovalents est alors entreprise et nous décrivons dans ce travail la structure d'une nouveau composé: Co-$(NH_4)_4(P_3O_9)_2.4H_2O$. La méthode de préparation est celle décrite pour le polytriphosphate de Cu^{II} (Jouini & Durif, 1983).

Partie expérimentale. Cristal: parallélépipède tronqué, $0,13 \times 0,16 \times 0,20$ mm; densité: méthode picno-métrique; appareillage: diffractomètre Philips PW 1100; monochromateur: graphite (radiation

Mo $K\alpha$); paramètres cristallins affinés à partir de 25 réflexions ($16 < 2\theta < 30°$); domaine de mesure: 3 à 35° (θ); type de balayage: ω; domaine de balayage: $(1,20 + 0,20\,\mathrm{tg}\theta)°$; vitesse de balayage: $0,03°$ s^{-1}; trois réflexions de référence: 340, $\overline{3}40$ et $3\overline{4}0$; variation négligeable; 3771 réflexions mesurées (h: $-13\rightarrow13$, k: $-23\rightarrow23$, l: $0\rightarrow14$); 1864 réflexions indépendantes; $R_{int} = 0,062$. Les intensités sont corrigées de Lorentz-polarisation; aucune correction d'absorption. La structure a été résolue en exploitant la fonction de Patterson et les synthèses de Fourier. Après élimination de 394 réflexions correspondant à $I < 3\sigma(I)$ et 20 réflexions faibles et mal mesurées, l'affinement basé sur F et utilisant les facteurs thermiques anisotropes a conduit à $R = 0,053$; $wR = 0,061$; $S = 2,457$. Un schéma de pondération unitaire a été utilisé; $(\Delta/\sigma) = 0,00$; $\Delta\rho_{max}$
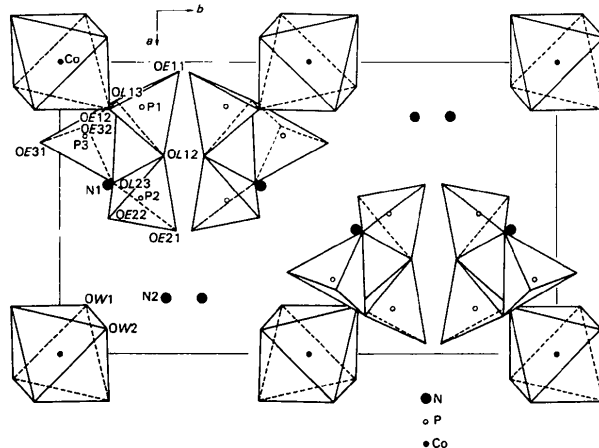

Fig. 1. Projection de la structure de $Co(NH_4)_4(P_3O_9)_2.4H_2O$ sur le plan (001).