

between the ligands of the GaI_2Re_2 nucleus, including the four equatorial CO ligands of the Re(3) atom, there exists for the phosphines [P(1) and P(2)] no alternative position in the polyhedra of the Re(1) and Re(2) central atoms. This can be proved by mutually exchanging the positions of the phosphine and CO ligands in a structure model of the title substance, where the phosphine phenyl groups become interlocked with the equatorial CO groups and free rotation of the phosphine ligands around their Re—P axis is prevented. Therefore, one factor with influence on the observed eclipsed arrangement of the CO ligand pairs around the Re(1)—Re(2) bond may be of steric origin.

A view around the Ga—Re(3) bond direction shows that the four CO ligands are staggered with respect to the positions of the four equatorial CO ligands of the Re(3) octahedron. The Ga atom with its three Re ligand atoms is situated at the centre of the eight CO ligands. This accumulation of atoms around the Lewis acid Ga^{III} has a screening effect and prevents a solvated species of the title substance from a typical addition reaction for a trivalent Ga atom with a Lewis base as has been proved with different halide ions.

Intermolecular distances do not indicate interactions exceeding van der Waals forces.

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

Re(1)—Re(2)	2.925 (1)	Mean values	
—I(1)	2.800 (1)	Re(1)—C	1.85 (2)
—I(2)	2.829 (2)	Re(2)—C	1.85 (2)
—Ga	2.531 (3)	Re(3)—C	1.94 (3)
—P1	2.414 (6)	P(1)—C	1.83 (2)
Re(2)—I(1)	2.820 (1)	P(2)—C	1.83 (1)
—I(2)	2.788 (2)	P(3)—C	1.82 (2)
—Ga	2.516 (2)	C—O	1.16 (3)
—P(2)	2.406 (5)		
Re(3)—Ga	2.494 (2)		
—P(3)	2.437 (6)		
Re(1)—I(1)—Re(2)	62.71 (3)	Ga—Re(1)—Re(2)	54.36 (5)
Re(1)—I(2)—Re(2)	62.76 (4)	Ga—Re(2)—I(1)	97.86 (6)
Re(1)—Ga—Re(2)	70.83 (6)	Ga—Re(2)—I(2)	99.91 (7)
Re(3)—Ga—Re(1)	144.1 (1)	Ga—Re(2)—Re(1)	54.81 (6)
Re(3)—Ga—Re(2)	144.8 (1)	P(1)—Re(1)—Re(2)	144.7 (1)
Ga—Re(1)—I(1)	98.04 (7)	P(2)—Re(2)—Re(1)	148.2 (1)
Ga—Re(1)—I(2)	98.48 (6)	P(3)—Re(3)—Ga	175.8 (1)

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Structures of Diguanidinium Tetrachloropalladate(II) and Guanidinium Tetrachloroaurate(III)

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Abstract. $2\text{CH}_6\text{N}_3^+.\text{PdCl}_4^{2-}$ (1), $M_r = 368.40$, tetragonal, $P4_2/n$, $a = 10.755$ (1), $c = 11.006$ (1) Å, $V = 1273.0$ (2) Å³, $Z = 4$, $D_m = 1.93$, $D_x = 1.94$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.24$ mm⁻¹, $F(000) = 720$, $T = 296$ K, final $R = 0.056$ for 1083 observed reflections. $\text{CH}_6\text{N}_3^+.\text{AuCl}_4^-$ (2), $M_r = 398.87$, monoclinic, $P2_1/c$, $a = 15.235$ (4), $b = 3.944$ (1), $c = 14.688$ (3) Å, $\beta = 94.60$ (2)°, $V = 879.7$ (4) Å³, $Z = 4$, $D_m = 3.00$, $D_x = 3.01$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 18.23$ mm⁻¹, $F(000) = 720$, $T = 296$ K, final $R = 0.056$ for 1161 observed

reflections. In (1) two planar guanidinium ions related by the center of symmetry lie close together with a C...C distance of 3.32 (1) Å. Such paired cations and square-planar PdCl_4^{2-} anions are in the alternate arrangement analogous to the NaCl structure, more adequately described by the (anti)pyrite FeS_2 -*p* structure. In (2) square-planar AuCl_4^- anions, like PdCl_4^{2-} in (1), construct the pseudo face-centered lattice, but the anion and cation are arranged in such a unique way that each cation is surrounded by four anions in a nearly square coordination and *vice versa*. In both structures all H atoms participate in N—H...Cl hydrogen bonding to form three-dimensional hydrogen-bonded frameworks.

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Introduction. Some early workers reported that guanidinium cations could form stable ionic crystals with complex anions such as tetrachloroaurate(III), -platinate(II) and -palladate(II) ions (Mellor, 1936). Both the cation, probably including H atoms, and the complex anions are planar but their sizes and shapes are different. It is therefore interesting to compare the crystal structures of these 1:1 and 2:1 ionic crystals with the typical NaCl (or CuCl) and CaF₂ (or K₂PtCl₄) structures, respectively. Furthermore, the guanidinium ion is capable of forming six hydrogen bonds by donating H atoms, while the complex anions act as hydrogen-bond acceptors *via* Cl⁻ ions. Such hydrogen-bond formation and the planarity of both ions must control their arrangements to some extent. In order to clarify these points, the crystal structures of the title compounds were determined by X-ray diffraction. Recently, ³⁵Cl NQR and ¹H NMR of these compounds were studied, providing valuable information on the crystal structures and molecular dynamics (Gima, Furukawa, Ikeda & Nakamura, 1983). In particular, the results of ³⁵Cl NQR serve to confirm the crystal structure of the aurate complex.

Experimental. Both compounds prepared by methods described in previous papers (Gima, Furukawa, Ikeda & Nakamura, 1983; Mellor, 1936) and recrystallized from dilute HCl solution. Densities measured pycnometrically. Experimental conditions and refinement details are summarized in Table 1.

Table 1. *Experimental conditions and refinement details*

	(1)	(2)
Crystal color, shape and size (mm)	Brown Cuboctahedron like 0.20 × 0.20 × 0.20	Yellow Needle 0.20 × 0.20 × 0.21
Diffractometer	Rigaku AFC-4	
Radiation	Graphite monochromated Mo K α	
Scan mode	ω -2 θ scan	
Number of reflections and 2 θ range (°) used for measuring lattice parameters	25 21 < 2 θ < 31	31 20 < 2 θ < 29
Max. $\sin \theta / \lambda$ (Å ⁻¹)	0.65	0.65
Range of h, k and l	0-14, $\bar{14}$ -14, 0-14	$\bar{19}$ -19, 0-5, $\bar{19}$ -19
Standard reflections	600, 006, 404	020, 424, 800
	No variations	
Number of reflections measured	3055	4209
Number of independent reflections	1459	2140
R_{int} on F	0.036	0.034
Number of observed reflections	1083	1179
Criterion for observed reflections	$F_o > 3\sigma(F_o)$	
Absorption correction	Experimental absorption correction based on ψ scan (North, Phillips & Mathews, 1968)	
Max. correction factors on F	1.031	1.133
Solution	Heavy-atom method	
Atomic scattering factors, f' and f''	International Tables for X-ray Crystallography (1974)	
Refinement method	Full matrix least-squares on F	
H atoms	From difference Fourier synthesis	Not located
Number of parameters	79	65
R (wR)	0.056 (0.036)	0.056 (0.041)
S	1.867	2.240
Weighting scheme	$1/\sigma^2(F_o)$	
Av., max. $1/\sigma$	0.04, 0.26	0.02, 0.12
Final residual electron densities (e Å ⁻³)	< 0.77	< 3.95

Compound (1). All non-H atoms refined anisotropically; positional parameters of H atoms allowed to vary but isotropic thermal parameters fixed.

Compound (2). Because of uncertain extinctions for $0k0$ reflections, systematic absences $l = 2n + l$ for $h0l$ reflections indicate possible space groups $P2_1/c$, $P2_1/c$ or Pc . The noncentrosymmetric Pc was chosen as the starting space group on the basis of the statistical distribution of the intensity data. Refinement with anisotropic thermal parameters for Au and Cl atoms and isotropic thermal parameters for C and N atoms converged to $R = 0.054$ ($wR = 0.054$) for 2004 Bijvoet-paired reflections with $|F_o| > 3\sigma(F_o)$. However, this space group gave large standard deviations and strong correlations among atomic parameters during refinements. The structure obtained had a pseudo center of symmetry at $(0, \frac{1}{4}, 0)$ and strongly suggested $P2_1/c$. The alternative refinement including H atoms with fixed theoretical positions [$N(sp^2)-H = 1.02$ Å] and $B_{iso} = 4.0$ Å² in $P2_1/c$ converged to $R = 0.056$ ($wR = 0.041$) for 1161 merged reflections. Eighteen low-angle reflections influenced by extinction were not included in the refinement. Although the refinement based on $P2_1/c$ did not give any significant improvement in the R index, the standard deviations of the atomic coordinates were reduced to about one-third of those obtained from the refinement based on Pc . The space group $P2_1/c$ was therefore chosen as the correct one by also taking into account the ³⁵Cl NQR results described later.

Computer programs used were *The Universal Crystallographic Computing System—Osaka* (1979), *RFINEII* (Finger, 1969), *UMBADTEA* (Finger, 1968) and *ORTEPII* (Johnson, 1976).

Discussion. Final positional and thermal parameters for (1) and (2) are given in Tables 2 and 3, respectively,* and selected interatomic distances and angles are given in Table 4. Stereoviews (Johnson, 1976) of crystal structures for (1) and (2) are shown in Figs. 1 and 2, and the projection of (2) along [010] in Fig. 3.

In both structures the Pd^{II} and two crystallographically independent Au^{III} atoms are located on crystallographic centers of symmetry and consequently each metal atom is surrounded by four Cl atoms in a perfect planar array. The coordination about the metals is approximately square planar, and the largest distortion from the ideal square geometry is found in the angles around Au(2) (Table 4). The Pd—Cl and Au—Cl bond lengths are in good agreement with those found in [cytosineH⁺]₂[PdCl₄²⁻] [2.298 (1) and 2.295 (1) Å] (Kinderg & Amma, 1975) and K[AuCl₄].2H₂O

* Lists of structure factors, anisotropic thermal parameters, mean planes and hydrogen parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42613 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

[2.285 (5) and 2.291 (6) Å] (Theobald & Omrani, 1980), respectively. The guanidinium cations are also planar within the experimental errors. The maximum deviations from the least-squares planes are 0.007 (7) Å for (1) and 0.01 (2) Å for (2). The H atoms in (1) lie on the cation plane with a maximum deviation of 0.24 (6) Å. The average C—N distances and N—C—N angles for (1) and (2) are 1.315 (9) Å and 120.0 (7)° and 1.30 (1) Å and 120 (1)°, respectively, these being in agreement with those in the literature, *cf.* (CH₆N₃)₂[B₄O₅(OH)₄].2H₂O [1.326 Å and 120.0° *av.*] (Weakley, 1985).

Both structures are characteristic with respect to the packing of ions. In (1) two guanidinium cations related by the center of symmetry lie close together. The C...C direction is nearly vertical (86.2°) to the guanidinium planes and therefore the interplanar separation (3.32 Å) is almost the same as the C...C distance of 3.32 (1) Å. This value is only slightly less than the van der Waals contact 3.6 Å, and very similar to the interlayer distance of 3.35 Å found in graphite. The two guanidinium cations are in pseudo $\bar{3}$ symmetry, which forces the N atoms to be located on the most distant sites. (1) is the first example of the pairing of guanidinium cations to the best of our knowledge. The centers of the paired guanidinium cations are located on the body center and edge centers of the face-centered

lattice formed by the complex anions PdCl₄²⁻. Thus, the centers of the anions and the cations are arranged in the same manner as Na⁺ and Cl⁻ ions in NaCl, and hence the structure is preferably regarded as a pyrite-like, FeS₂-*p*, structure. In (2), AuCl₄⁻ anions also construct a pseudo face-centered lattice like the PdCl₄²⁻ anions of (1). However, the arrangement of anions and cations is neither the NaCl nor the CuCl structure but a unique one. The cations occupy four of the eight octants of the cell formed by anions in such a way that the four central C atoms have two sets of similar *y* coordinates along the *c* axis. Each cation is hydrogen bonded to six Cl atoms of the four complex anions in a nearly square (not tetrahedral) coordination, owing to the planar geometries of both ions, including H atoms. Such a unique arrangement produces tunnel-like cavities along the *c* direction, as seen in Fig. 2.

Table 2. Final coordinates ($\times 10^4$) and isotropic thermal parameters (Å²) for (1)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} / <i>B</i> _{iso}
Pd	0	0	0	3.558 (7)*
Cl(1)	-177 (2)	-1457 (1)	1503 (1)	6.58 (2)*
Cl(2)	-1352 (1)	1271 (2)	1027 (2)	5.69 (3)*
C	3800 (6)	592 (6)	749 (6)	4.4 (1)*
N(1)	3393 (5)	-491 (5)	1105 (5)	5.2 (1)*
N(2)	4612 (7)	1202 (6)	1423 (7)	6.5 (1)*
N(3)	3390 (6)	1100 (5)	-266 (6)	5.4 (1)*
H(1)	2972 (57)	-971 (55)	569 (55)	6.0
H(2)	3703 (55)	-1116 (57)	1655 (59)	7.5
H(3)	5050 (60)	1750 (63)	1185 (69)	7.0
H(4)	4941 (54)	958 (57)	1985 (52)	4.0
H(5)	3652 (64)	1724 (62)	-545 (61)	7.5
H(6)	2953 (57)	726 (56)	-704 (57)	5.9

$$* B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

Table 3. Final coordinates ($\times 10^4$) and isotropic thermal parameters (Å²) for (2)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} / <i>B</i> _{iso}
Au(1)	0	0	0	1.92 (3)*
Au(2)	5000	0	5000	2.11 (4)*
Cl(1)	1481 (3)	1068 (16)	135 (3)	3.22 (14)*
Cl(2)	109 (3)	-2182 (20)	-1433 (3)	3.65 (15)*
Cl(3)	3602 (3)	1584 (18)	5279 (3)	3.49 (14)*
Cl(4)	5244 (3)	-2194 (19)	6442 (3)	3.56 (14)*
C	7512 (13)	2345 (44)	2400 (12)	2.5 (3)
N(1)	7547 (11)	3224 (58)	1554 (11)	4.2 (4)
N(2)	6790 (12)	2942 (61)	2798 (11)	4.5 (4)
N(3)	8160 (11)	816 (48)	2842 (11)	3.9 (4)

$$* B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j.$$

Table 4. Selected interatomic distances (Å) and angles (°)

(1) [C(NH ₂) ₃] ₂ [PdCl ₄]			
(a) Anion and cation			
Pd—Cl(1)	2.287 (2)	Pd—Cl(2)	2.294 (2)
C—N(1)	1.304 (8)	C—N(2)	1.321 (9)
C—N(3)	1.319 (9)		
Cl(1)—Pd—Cl(2)	89.95 (6)	Cl(1)—Pd—Cl(2)	90.05 (6)
N(1)—C—N(2)	119.8 (6)	N(1)—C—N(3)	120.8 (6)
N(2)—C—N(3)	119.4 (6)		

(b) Hydrogen bonding				
A—H...B	A...B	A—H	H...B	∠A—H...B
N(1)—H(1)...Cl(2 ⁱⁱ)	3.320 (6)	0.90 (6)	2.49 (6)	152 (5)
N(1)—H(2)...Cl(2 ⁱⁱⁱ)	3.310 (6)	0.96 (6)	2.56 (7)	134 (5)
N(2)—H(3)...Cl(2 ⁱⁱⁱ)	3.329 (7)	0.80 (7)	2.55 (7)	164 (7)
N(2)—H(4)...Cl(1 ^{iv})	3.368 (7)	0.76 (6)	2.63 (6)	165 (6)
N(3)—H(5)...Cl(1 ^{iv})	3.337 (6)	0.79 (7)	2.55 (7)	171 (6)
N(3)—H(6)...Cl(2 ⁱ)	3.465 (6)	0.78 (6)	2.78 (6)	148 (6)

Symmetry code: (i) $-x, -y, -z$; (ii) $\frac{1}{2}-y, x, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, z$; (iv) $\frac{1}{2}+x, \frac{1}{2}+y, -z$.

(2) [C(NH ₂) ₃][AuCl ₄]			
(a) Anion and cation			
Au(1)—Cl(1)	2.288 (5)	Au(1)—Cl(2)	2.293 (6)
Au(2)—Cl(3)	2.288 (6)	Au(2)—Cl(4)	2.291 (6)
C—N(1)	1.30 (3)	C—N(2)	1.31 (3)
C—N(3)	1.29 (3)		
Cl(1)—Au(1)—Cl(2)	90.3 (2)	Cl(1)—Au(1)—Cl(2)	89.7 (2)
Cl(3)—Au(2)—Cl(4)	91.3 (2)	Cl(3)—Au(2)—Cl(4 ^{iv})	88.7 (2)
N(1)—C—N(2)	119 (2)	N(1)—C—N(3)	121 (2)
N(2)—C—N(3)	120 (2)		

(b) Estimated hydrogen bonding (H...Cl < 2.80 Å and ∠A—H...B > 130°)

A—H...B	A...B	H...B	∠A—H...B
N(1)—H(1)...Cl(3 ⁱⁱⁱ)	3.36 (2)	2.45	146
N(1)—H(2)...Cl(1 ^{iv})	3.44 (2)	2.62	136
N(1)—H(2)...Cl(2 ^{iv})	3.61 (2)	2.73	143
N(2)—H(3)...Cl(3 ⁱⁱⁱ)	3.44 (2)	2.46	158
N(2)—H(4)...Cl(4 ^v)	3.40 (2)	2.38	170
N(3)—H(5)...Cl(2 ^{iv})	3.52 (2)	2.61	147
N(3)—H(6)...Cl(1 ⁱⁱⁱ)	3.52 (2)	2.58	152

Symmetry code: (i) $-x, -y, -z$; (ii) $1-x, -y, 1-z$; (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, -y, -z$; (v) $x, \frac{1}{2}-y, -\frac{1}{2}+z$.

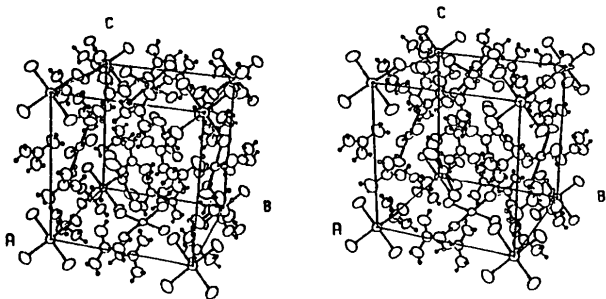


Fig. 1. Stereoscopic drawing of the crystal structure for (1).

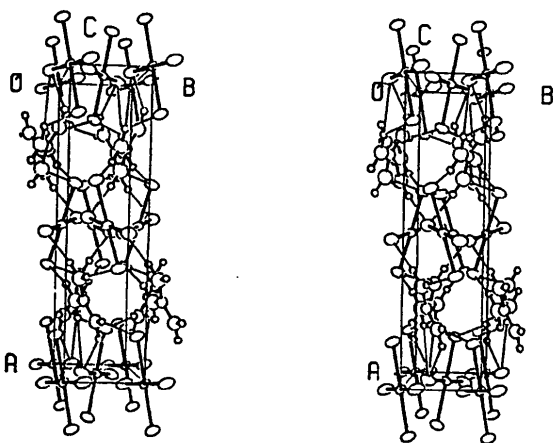
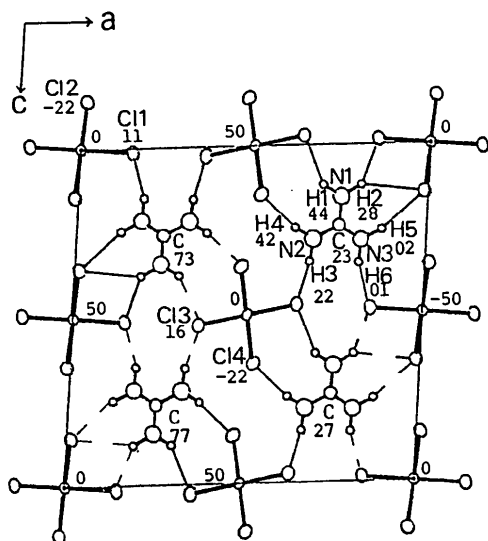


Fig. 2. Stereoscopic drawing of the crystal structure for (2).

Fig. 3. Projection of (2) along [010] with atom numbering and y coordinates ($\times 10^2$).

In both structures the cations are connected to any adjacent anions by $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds, in addition to electrostatic interactions. All H atoms contribute to form the three-dimensional hydrogen-bonded frameworks (Table 4).

The present X-ray results are consistent with those of ^{35}Cl NQR studies. For (1) two nonequivalent Cl atoms with relatively large thermal parameters at 296 K are responsible for the two ^{35}Cl NQR frequencies having an equal intensity in the temperature range 77–220 K. A comparison of the Pd–Cl bond lengths and also the hydrogen-bonding schemes suggests that the bonding of Cl(2) is more ionic than Cl(1) and consequently the lower-frequency signal (16.30 MHz at 77 K) is assignable to the Cl(2) atom. On the other hand, the fact that (2) contains two independent complex anions and their four nonequivalent Cl atoms with small thermal parameters is compatible with the NQR results, in which four lines are detected at temperatures between 77 and 344 K and two definite groups of temperature dependences of ^{35}Cl NQR frequencies and spin–lattice relaxation times, T_1 , are distinguished (Furukawa & Nakamura, 1986). Finally, it should be noted that the refinement with the non-centrosymmetric space group Pc might be affected by ‘inverse overlap’ as in KAuCl_4 (Bonamico & Dessy, 1973), but this space group is in conflict with the structural information obtained from the NQR measurement.

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