

Acta Cryst. (1969). **B25**, 1203

The crystal structure of *trans*-bisglycinatoplatinum(II), Pt(NH₂CH₂COO)₂. By H. C. FREEMAN and M. L. GOLOMB, *School of Chemistry, University of Sydney, Sydney 2006, Australia*

(Received 15 January 1969)

The structure of the *trans* isomer of bisglycinatoplatinum(II) has been determined from three-dimensional data. The crystals are triclinic with $a=5.322$, $b=4.169$, $c=8.332$ Å, $\alpha=99.88^\circ$, $\beta=98.04^\circ$, $\gamma=104.44^\circ$, $Z=1$, space group $P\bar{1}$. The metal-donor bond lengths are Pt-N(amino)=2.04, Pt-O(carboxyl)=2.00 Å, and the angle N(amino)-Pt-O(carboxyl)=82.5°.

Glycine (GlyH=NH₂CH₂COOH) forms several types of complexes with Pt^{II} ions. Reaction of the anionic ligand with potassium tetrachloroplatinate(II) (Grinberg & Ptitzuin, 1932; Grinberg & Volshtein, 1941) yields the complex Pt(Gly)₂ in which the ligand molecules act as bidentate chelates. A mechanism for the reaction has been postulated (Grinberg & Volshtein, 1935). The interconversion of the *cis* and *trans* isomers of Pt(Gly)₂ has been investigated (Volshtein, Mogilevkina & Motyagina, 1961; Volshtein & Volodina, 1962). Reaction of Pt(Gly)₂ with hydrochloric acid yields successively Pt(Gly)(GlyH)Cl and Pt(GlyH)₂Cl₂ (Grinberg & Ptitzuin, 1932; Volshtein & Volodina, 1960). In the presence of excess ligand, Pt(Gly)₂(GlyH)₂ and salts of Pt(Gly)₃⁻ and Pt(Gly)₄²⁻ can be isolated (Grinberg & Volshtein, 1935; Volshtein & Motyagina, 1960). Monodentate glycine presumably coordinates through the N(amino) atom. Infrared spectra for many of these complexes have been reported (Rosenberg, 1956; Varshavskii, In'kova & Grinberg, 1963) and force constants for the metal-ligand bonds have been calculated (Condrate & Nakamoto, 1965). Many complexes of Pt^{II} with other amino acids have been prepared. The ligands include α - and β -alanine (Grinberg & Volshtein, 1937; Volshtein & Mogilevkina, 1955), methionine (Volshtein & Mogilevkina, 1962, 1963, 1965) and histidine (Nelson & Frye, 1966; Volshtein & Luk'yanova, 1966).

The tetracyanoplatinate(II) anion, dichloroethylenediamineplatinum(II) and *cis*-bisglycinatoplatinum(II) have been used to prepare isomorphous heavy atom derivatives used in the structure analyses of the proteins ribonuclease-A (Kartha, Bello & Harker, 1967) and ribonuclease-S (Wyckoff, Hardman, Allewell, Inagami, Johnson & Richards, 1967). The present structure analysis is the first of a proposed series in which the interaction of Pt^{II} with amino acids and peptides is to be explored, in order to set up geometrical criteria for Pt-binding sites in proteins.

Crystals of the *trans* isomer of bisglycinatoplatinum(II) were prepared by the method of Pinkard, Sharratt, Wardlaw & Cox (1934). Counter data from crystals mounted about two different axes were used to obtain accurate unit-cell dimensions. Values of θ for ninety high-angle reflexions on both zero and upper layers were used to fit the cell dimensions to a function of $\sin^2 \theta$ by a least-squares procedure. The crystal system is triclinic, and the space group $P\bar{1}$ or $P\bar{1}$. The density indicates that there is one formula unit per unit cell and hence, for space group $P\bar{1}$, the Pt atom must lie on a centre of symmetry. A Delaunay reduction of the unit cell (transformation: $\mathbf{a}'=\mathbf{a}-\mathbf{b}$, $\mathbf{b}'=\mathbf{b}$, $\mathbf{c}'=\mathbf{c}$) was performed. The crystal data for the reduced cell are given in Table 1.

Intensity data were collected about two axes, a and b , of the non-reduced cell. The layers collected were $0kl-4kl$ and $h0l-h4l$. The data were collected on a Supper equi-

Table 1. *Dimensions of the reduced cell of Pt(Gly)₂*

Standard deviations are estimated to be 0.1%.

C ₄ H ₈ N ₂ O ₄ Pt	<i>F.W.</i> = 343.3
$a=5.322$ Å	$\alpha=99.88^\circ$
$b=4.169$	$\beta=98.04$
$c=8.332$	$\gamma=104.44$
$V=172.9$ Å ³	$Z=1$
$D_m=3.1$ g.cm ⁻³	$D_x=3.30$ g.cm ⁻³
$\lambda(\text{Cu } K\alpha_1)=1.54051$ Å	$\mu_{\text{Cu}K\alpha}=399$ cm ⁻¹
$\lambda(\text{Cu } K\alpha_2)=1.54433$	$F(000)=156$ e

inclination diffractometer which had been automated for control by a PDP-8/S computer (Freeman, Guss, Nockolds, Page & Webster, 1969). Intensities were measured by the ' ω -scan' method at the rate of 3 deg.min⁻¹, with a counter aperture of 2°30'. It was verified that the aperture was correct when subsequent calculation showed that the interlayer scale factors were all very close to unity. For each layer, the equi-inclination angles, μ and ν , were set manually. The computer generated the indices, calculated the counter- and crystal-settings and scan-range for each reflexion, and controlled the operation of the motors and counter. Background counts were made before and after scanning through each intensity maximum. A sufficiently large imbalance in the background counts caused a reflexion to be remeasured with an increased scan-range.

After correction for Lorentz and polarization factors as well as for absorption (Coppens, Leiserowitz & Rabino- vich, 1965), the two data sets were scaled together by the method of Rae (1965; Rae & Blake, 1966). After scaling, the agreement index, R , between the two independently recorded sets of data was 0.018, R being defined as

$$\left\{ \frac{\sum_h \sum_i k_i^{-2} (\bar{F}_h - k_i F_{hi})^2}{\sum_h \sum_i F_{hi}^2} \right\}^{1/2}$$

(where k_i represents the calculated scale-factor applied to the observation F_{hi} of the h th reflexion on the i th layer, and \bar{F}_h is the mean value of the h th structure amplitude). All 611 independent reflexions within the accessible angular range were above background level.

The structure was solved by the heavy-atom Fourier method and the parameters were refined by full-matrix, non-linear least squares using a modification of the program *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w_j |F_o| - |F_c|^2$. The scattering factors used were those of Cromer & Waber (1965) for the Pt²⁺ ion and the O, N, and C atoms. A correction was applied for the anomalous dispersion caused by the platinum atom (Cromer, 1965). The final refinement included anisotropic temperature factors for all atoms. The inclusion of anisotropic thermal parameters for the light atoms was statistically justified at the 95% confidence level (Hamilton, 1964).

were given weights

$$w = \{1 - \exp[-2(\sin \theta/\lambda - 0.06)^2]\} / \{168.9 - 2.15|F_o| + 0.0072|F_o|^2\}.$$

The final residuals were

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.024$$

and

$$R_2 = [\Sigma w|F_o| - |F_c||^2]^{1/2} / \Sigma w|F_o| = 0.018.$$

The observed and calculated structure factors are listed in Table 2, and the final atomic parameters are given in Table 3. For the light atoms, the statistical standard deviations of the positions are all less than 0.006 Å.

The structure consists of a platinum atom bound by two bidentate glycine residues in a square-planar *trans* configuration. The coordination differs from that in the corresponding nickel (Freeman & Guss, 1968) and copper (Freeman, Snow, Nitta & Tomita, 1964) complexes in that the fifth and sixth coordination positions are vacant. The dimensions of the glycine residues in these three complexes are almost identical, and are very similar to those of the free ligand (Marsh, 1958). These dimensions are compared in Table 4.

In amino-acid complexes, a linear relationship has been observed between the mean metal-ligand bond-length and the angle subtended by the donor atoms at the metal (Freeman, 1967). The N(amino)-Pt-O(carboxyl) angle in Pt(Gly)₂ (82.5°) agrees well with the value (83°) predicted for a mean metal-donor bond-length of 2.0 Å.

The carboxyl group is planar within two standard deviations of the relevant atomic positions. The Pt and N atoms lie +0.05 and -0.32 Å from the carboxyl plane, respectively [compared with deviations of +0.26 and +0.61 Å in Ni(Gly)₂(OH₂)₂]. The dihedral angle about the C(1)-C(2) bond [*i.e.* the angle between the normals to the planes through N, C(1), C(2) and C(1), C(2), O(1)] is 13.7°.

The structure is shown in Fig. 1. Each molecule of the complex Pt(Gly)₂ takes part in eight hydrogen bonds, two to each of the four surrounding complexes obtained by translations of one unit-cell in the ±x and ±(x+y) directions (Table 5). There is no intermolecular bonding in the z direction.

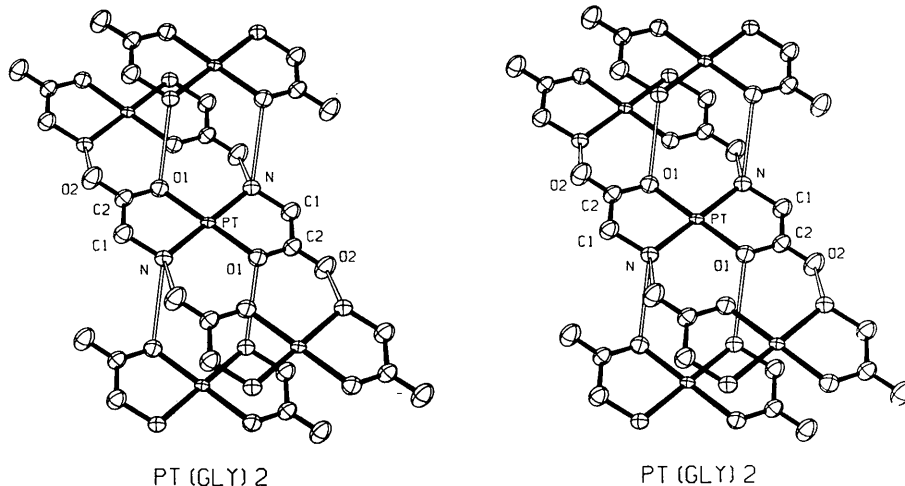


Fig. 1. Stereoscopic diagram for Pt(Gly)₂, showing ellipsoids of thermal vibration drawn at the 59% probability level. Hydrogen bonds are not shaded.

Table 5. *Hydrogen bonds in Pt(Gly)₂*

E.s.d.'s in parentheses.

Superscripts: ' = atom at (-1+x, y, z)
 '' = atom at (-1+x, -1+y, z)
 ''' = atom at (1+x, y, z)
 iv = atom at (1+x, 1+y, z)

		Bond-lengths
N···O(1')	O(1)···N'''	2.971 (6) Å
N···O(2'')	O(2)···N ^{iv}	2.895 (6)
		Bond-angles at H-bonded atoms
Pt—N·····O(1')		126.5 (2)°
Pt—N·····O(2'')		120.2 (2)
C(1)—N·····O(1')		116.6 (3)
C(1)—N·····O(2'')		103.8 (3)
O(1')···N·····O(2'')		74.6 (2)
Pt—O(1)···N'''		115.9 (3)
C(2)—O(1)···N'''		106.7 (3)
C(2)—O(2)···N ^{iv}		117.7 (3)

This research was supported by the National Institute for General Medical Sciences, U.S. Public Health Service (Grant GM-10867), and by the Australian Research Grants Committee (Grant 65/15552).

References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). Report ORNL-TM-305, Oak Ridge National Laboratory, Tennessee.
- CONDRADE, R. A. & NAKAMOTO, K. (1965). *J. Chem. Phys.* **42**(7), 2590.
- COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
- FREEMAN, H. C. (1967). *Advanc. Protein Chem.* **22**, 257.
- FREEMAN, H. C. & GUSS, J. M. (1968). *Acta Cryst.* **B24**, 1133.
- FREEMAN, H. C., GUSS, J. M., NOCKOLDS, C. E., PAGE, R. & WEBSTER, A. (1969). Paper in preparation.

- FREEMAN, H. C., SNOW, M. R., NITTA, I. & TOMITA, K. (1964). *Acta Cryst.* **17**, 1463.
- GRINBERG, A. A. & PITTZUIN, B. V. (1932). *Ann. Inst. Platine*, **9**, 55.
- GRINBERG, A. A. & VOLSHEIN, L. M. (1935). *C. R. Acad. Sci. URSS*, **7**, 485.
- GRINBERG, A. A. & VOLSHEIN, L. M. (1937). *Bull. acad. sci. URSS, Classe sci. math. nat., Ser. Chim.* 885.
- GRINBERG, A. A. & VOLSHEIN, L. M. (1941). *Bull. acad. sci. URSS. Classe sci. chim.* 381.
- HAMILTON, W. C. (1964). *Statistics in Physical Science*, p. 157. New York: Ronald Press.
- HOARD, L. C. & JACOBSON, R. A. (1966). *J. Chem. Soc. (A)*, p. 1203.
- KARTHA, G., BELLO, J. & HARKER, D. (1967). *Nature, Lond.* **213**, 862.
- MARSH, R. E. (1958). *Acta Cryst.* **11**, 654.
- NELSON, D. & FRYE, H. (1966). *Z. Naturforsch.* **b21**, 630.
- PINKARD, F. W., SHARRATT, E., WARDLAW, W. & COX, E. G. (1934). *J. Chem. Soc.* p. 1012.
- RAE, A. D. (1965). *Acta Cryst.* **19**, 683.
- RAE, A. D. & BLAKE, A. B. (1966). *Acta Cryst.* **20**, 586.
- ROSENBERG, A. (1956). *Acta Chem. Scand.* **10**, 840.
- VARSHAVSKII, Y. S., IN'KOVA, E. N. & GRINBERG, A. A. (1963). *Zh. Neorgan. Khim.* **8**, 2659.
- VOLSHEIN, L. M. & LUK'YANOVA, I. G. (1966). *Russ. J. Inorg. Chem.* **11**, 708.
- VOLSHEIN, L. M. & MOGILEVKINA, M. F. (1955). *Dokl. Akad. Nauk SSSR*, **104**, 418.
- VOLSHEIN, L. M. & MOGILEVKINA, M. F. (1962). *Dokl. Akad. Nauk SSSR*, **142**, 1305.
- VOLSHEIN, L. M. & MOGILEVKINA, M. F. (1963). *Russ. J. Inorg. Chem.* **8**, 304.
- VOLSHEIN, L. M. & MOGILEVKINA, M. F. (1965). *Russ. J. Inorg. Chem.* **10**, 293.
- VOLSHEIN, L. M., MOGILEVKINA, M. F. & MOTYAGINA, G. G. (1961). *Russ. J. Inorg. Chem.* **6**, 564.
- VOLSHEIN, L. M. & MOTYAGINA, G. G. (1960). *Russ. J. Inorg. Chem.* **5**, 840.
- VOLSHEIN, L. M. & VOLODINA, I. O. (1960). *Russ. J. Inorg. Chem.* **5**, 949.
- VOLSHEIN, L. M. & VOLODINA, I. O. (1962). *Russ. J. Inorg. Chem.* **7**, 1399.
- WYCKOFF, H. W., HARDMAN, K. D., ALLEWELL, N. M., INAGAMI, T., JOHNSON, L. N. & RICHARDS, F. M. (1967). *J. Biol. Chem.* **242**, 3984.

Acta Cryst. (1969). **B25**, 1206

The $D1_3$ structure type in intermetallic compounds. By GIACOMO BRUZZONE, *Institute of Physical Chemistry, Genoa University, Genoa, Italy*

(Received 29 July 1968 and in revised form 24 October 1968)

As part of a study of the MX_4 intermetallic compounds the crystal structures of the following have been investigated: $NaGa_4$, $NaIn_4$, $NaSn_4$, KGa_4 , KIn_4 , KTI_4 , KSn_4 , $RbIn_4$ and $CsIn_4$. Results were only obtained for the compounds $NaGa_4$, KGa_4 , KIn_4 and $RbIn_4$. A survey is presented of the available data on other MX_4 phases formed by elements of groups I-III A with groups II-IV B. It is concluded that the formation of MX_4 phases depends on the position of the element X in the periodic system rather than the atomic size factor or the valency of M.

Continuing the investigation on the crystal structure of the MX_4 intermetallic compounds (Bruzzone, 1965), the behaviour of the alkali metals Na, K, Rb, Cs was examined. Samples of the following compositions were prepared: $NaGa_4$, $NaIn_4$, $NaSn_4$, KGa_4 , KIn_4 , KTI_4 , KSn_4 , $RbIn_4$, $CsIn_4$.

The metals used were Na, K, Rb, Cs: 99.9%; Ga, In, Tl, Sn: 99.99%, pure. The alloys were obtained by direct synthesis from stoichiometric quantities of the two metals, melted in sealed Pyrex tubes under a low-pressure atmosphere of very pure argon. The samples were heated to complete fusion and the cooling pattern was dictated by the characteristics of the corresponding phase diagram; for those cases in which the diagram was unknown, the samples were very slowly cooled to room temperature.

All the alloys being very oxidizable, it was necessary to handle them in an inert-gas atmosphere: the specimens for metallographic examination were kept under anhydrous paraffin oil and those for X-ray analysis were sealed in glass capillaries under vacuum. Only $NaIn_4$, KTI_4 and $CsIn_4$ among the prepared alloys appeared to be heterogeneous. The X-ray analysis was not successful in the cases of $NaSn_4$ and KSn_4 , which gave very complex powder patterns. However, it was possible to separate needle-shaped single crystals of KGa_4 and to demonstrate the

orthorhombic symmetry of this phase. The following lattice constants were obtained by rotation and Weissenberg photographs: $a_0 = 13.86$, $b_0 = 16.02$, $c_0 = 6.49$ Å.

The tetragonal $D1_3(BaAl_4)$ structure-type was found for the phases: $NaGa_4$, KIn_4 and $RbIn_4$. From powder photographs the lattice constants were calculated by the least-squares method and these are listed in Table 1 together with the z parameters obtained by comparison of the calculated and observed intensities of the reflexions.

Table 1. *Lattice constants and z parameters*

Compound	a_0	c_0	c_0/a_0	z
$NaGa_4$	4.223 Å	11.19 Å	2.65	0.381
KIn_4	4.835	12.71	2.63	0.379
$RbIn_4$	4.914	12.82	2.61	0.378

A survey of the available data on the MX_4 phases, formed by an element of the groups IA, IIA, IIIA (rare earth and thorium metals) as component M, with a IIB, IIIB, IVB group element of the periodic system as component X, yields the following information.

(a) MX_4 compounds with X = IIB group element

The alkali, alkaline earth and rare earth metals do not form 1:4 phases with zinc and cadmium. Thorium gives a