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Structural Characterization of Tetramethylammonium Pentakis(trichlorogermanyl)platinate(II)

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The crystal and molecular structure of tetramethylammonium pentakis(trichlorogermanyl)platinate(II), $(NMe_4)_3Pt(GeCl_3)_5$, has been determined from three-dimensional X-ray data collected by counter methods. The material crystallizes in the space group $P2_1/c$ of the monoclinic system with four molecules in a cell of dimensions $a = 11.300$ (9), $b = 14.982$ (16), $c = 25.631$ (28) Å, and $\beta = 100.81$ (5)°. The observed and calculated densities are 2.04 and 2.046 g cm^{-3}, respectively. Least-squares refinement of the structure has yielded a final value for the conventional R factor (on F) of 0.054 for 3091 independent reflections having $F^2 > 3\sigma(F^2)$. The $Pt(GeCl_3)_5{}^{3-}$ anion is a distorted trigonal bipyramid, the equatorial Pt–Ge bond distances being 2.424 (3), 2.399 (3), and 2.480 (3) Å, and the apical Pt–Ge bond distances being 2.410 (3) and 2.391 (3) Å. The bond angles at Pt in the plane are 111.09 (10), 141.46 (10), and 107.45 (10)°, the bond angle subtended at Pt by the apical Ge's being 175.66 (14)°. Thus, the anion is apparently much more severely distorted than the analogous tin ion $[Pt(SnCl_3)_5]^{3-}$.

Introduction

The syntheses of platinum-germanium chloride complexes have been reported[1] recently by Wittle and Urry, but according to these workers it was not possible to prepare a platinum-germanium chloride ion with a charge of −3. Jicha and Rivella,[2] however, report the preparation of a complex of stoichiometry $[Pt(GeCl_3)_5]^{3-}$, which is of great interest since it does have a charge of −3 and also because five-coordinate homogeneous ligand systems are still uncommon.

The first well-established example of a five-coordinate Pt species containing only monodentate ligands was $[(C_6H_5)_3PCH_3]_3[Pt(SnCl_3)_5]$, whose structure was reported by Cramer, *et al.*;[3] the only two other five-coordinate Pt(II) complexes which had been isolated at that time had highly stabilizing polydentate ligands.[3] Johnson, Shriver, and Shriver[4] report that there is no measurable difference in the Lewis base strength of $GeCl_3{}^-$ and $SnCl_3{}^-$, and Jetz and Graham[5] also report that $SiCl_3{}^-$, $SnCl_3{}^-$, and $GeCl_3{}^-$ have similar Lewis basicities. Hence, it is reasonable that a $GeCl_3$ analog of the $Pt(SnCl_3)_5{}^{3-}$ ion should exist.

In order to further characterize the $[Pt(GeCl_3)_5]^{3-}$ species and to compare it with the tin analog, and also in order to further our understanding of metal-germanium bonds, we have undertaken a three-dimensional structural study of the tetramethylammonium salt of this ion.

Experimental Section

Red, needle-shaped crystals under an inert atmosphere were generously prepared and donated by Professor D. C. Jicha. When exposed to air, these crystals remained unchanged for at least 1 hr but showed noticeable decomposition within 5 hr. The crystal used for data collection was coated with nail polish in an attempt to preserve it, and there were no signs of decomposition during the data collection.

Table I. Positional Parameters for $[N(CH_3)_4]_3Pt(GeCl_3)_5$

Atom	*x*	*y*	*z*
Pt	0.2043 (1)	0.2275 (1)	−0.1173 (0)
Ge(1)	0.1923 (2)	0.1624 (2)	−0.0330 (1)
Ge(2)	0.1027 (2)	0.2279 (2)	−0.2094 (1)
Ge(3)	0.3781 (2)	0.3310 (2)	−0.1096 (1)
Ge(4)	0.3239 (2)	0.1008 (2)	−0.1333 (1)
Ge(5)	0.0744 (2)	0.3455 (1)	−0.1001 (1)
Cl(1)	0.1915 (7)	0.0175 (4)	−0.0229 (3)
Cl(2)	0.3382 (6)	0.3016 (5)	−0.4662 (2)
Cl(3)	0.0391 (7)	0.3135 (5)	−0.4933 (3)
Cl(4)	0.2055 (7)	0.2825 (5)	−0.2667 (2)
Cl(5)	0.0501 (7)	0.1021 (5)	−0.2510 (3)
Cl(6)	−0.0682 (8)	0.2962 (7)	−0.2385 (3)
Cl(7)	−0.4324 (6)	0.2855 (5)	−0.1068 (3)
Cl(8)	0.4205 (6)	0.4187 (5)	−0.0390 (3)
Cl(9)	0.3822 (6)	0.4381 (5)	−0.1696 (3)
Cl(10)	0.4230 (6)	0.1129 (5)	−0.1978 (2)
Cl(11)	−0.2359 (7)	0.4731 (4)	−0.3445 (3)
Cl(12)	0.4700 (6)	0.0596 (5)	−0.0699 (2)
Cl(13)	0.0713 (6)	0.4651 (4)	−0.1488 (3)
Cl(14)	0.1041 (6)	0.4114 (4)	−0.0234 (2)
Cl(15)	−0.1179 (5)	0.3169 (4)	−0.1065 (3)
N(1)	0.2927 (17)	0.0743 (12)	−0.3665 (6)
C(11)	0.2843 (22)	0.0050 (15)	−0.3217 (9)
C(12)	0.3233 (26)	0.0297 (23)	−0.4152 (10)
C(13)	0.1698 (21)	0.1189 (21)	−0.3823 (10)
C(14)	0.3881 (24)	0.1467 (17)	−0.3461 (12)
N(2)	−0.2507 (19)	0.2095 (14)	−0.4324 (9)
C(21)	−0.2135 (32)	0.1413 (26)	−0.4690 (13)
C(22)	−0.2986 (40)	0.2952 (19)	−0.4618 (15)
C(23)	−0.3568 (20)	0.1635 (25)	−0.4102 (15)
C(24)	−0.1526 (28)	0.2356 (30)	−0.3860 (12)
N(3)	−0.2055 (21)	0.0196 (15)	−0.1490 (7)
C(31)	−0.2931 (36)	−0.0526 (24)	−0.1405 (17)
C(32)	−0.0766 (28)	−0.0177 (29)	−0.1402 (14)
C(33)	−0.2235 (44)	0.0973 (22)	−0.1191 (17)
C(34)	−0.2478 (39)	0.0405 (30)	−0.2087 (13)

On the basis of Weissenberg and precession photographs the crystals were assigned to the monoclinic system. The observed systematic absences are $h0l$ for l odd and $0k0$ for k odd, which suggests that the space group is $P2_1/c$ ($C_{2h}{}^5$). The lattice constants, obtained by the least-squares method of Busing and Levy,[6] are $a = 11.300$ (9), $b = 14.982$ (16), $c = 25.631$ (28) Å, and $\beta = 100.81$ (5)°. A density of 2.046 g cm^{-3} calculated for four formula units in the cell agrees well with the value of 2.04 (1) g cm^{-3} obtained by flotation in dichloromethane–iodomethane mixtures.

Diffraction data were collected at 22° with the wavelength assumed as $\lambda(Mo\ K\alpha_1) = 0.7093$ Å using a Picker four-circle automatic diffractometer. A rectangular box-shaped crystal with faces (100), $(\bar{1}00)$, $(0\bar{1}1)$, $(01\bar{1})$, (011), and $(0\bar{1}\bar{1})$ was chosen. The distance between the (100) and $(\bar{1}00)$ faces was 0.815 mm, the distance between the $(0\bar{1}1)$ and $(01\bar{1})$ faces was 0.125 mm, and that between the (011) and $(0\bar{1}\bar{1})$ faces was 0.187 mm. The crystal was mounted on a glass fiber roughly parallel to the $(0\bar{1}1)$ face, and in this orientation intensity data were collected. The mosaicity of the crystal was examined by means of the narrow-source, open-counter ω-scan technique.[7] Since the general shape of the ω scans was symmetric and unsplit, we are confident that this is a single crystal.

Twelve reflections, accurately centered through a narrow vertical

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[1] J. K. Wittle and G. Urry, *Inorg. Chem.*, 7, 560 (1968).

[2] L. Rivella, Ph.D. Dissertation, University of North Carolina, 1969.

[3] R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 87, 658 (1965).

[4] M. P. Johnson, D. F. Shriver, and S. A. Shriver, *J. Amer. Chem. Soc.*, 88, 1588 (1966).

[5] W. A. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, 89, 2773 (1967).

[6] W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 22, 457 (1967).

[7] T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

Table II. Thermal Parameters for $[N(CH_3)_4]_3Pt(GeCl_3)_5$

Atom	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.00477 (8)	0.00268 (4)	0.00086 (1)	0.00019 (5)	0.00041 (2)	−0.00009 (2)
Ge(1)	0.00718 (25)	0.00328 (13)	0.00125 (4)	0.00017 (14)	0.00107 (8)	0.00026 (6)
Ge(2)	0.00756 (25)	0.00500 (14)	0.00096 (4)	0.00004 (17)	0.00014 (8)	−0.00041 (7)
Ge(3)	0.00558 (23)	0.00390 (13)	0.00124 (4)	−0.00099 (14)	0.00044 (8)	−0.00021 (6)
Ge(4)	0.00704 (26)	0.00360 (14)	0.00152 (5)	0.00123 (15)	0.00075 (9)	−0.00031 (6)
Ge(5)	0.00638 (24)	0.00307 (12)	0.00123 (4)	0.00059 (14)	0.00040 (8)	−0.00006 (6)
Cl(1)	0.01516 (91)	0.00344 (33)	0.00243 (15)	0.00003 (44)	0.00155 (28)	0.00055 (18)
Cl(2)	0.01322 (82)	0.00759 (48)	0.00149 (12)	0.00191 (49)	0.00001 (24)	−0.00037 (19)
Cl(3)	0.01562 (95)	0.00719 (45)	0.00261 (16)	−0.00273 (53)	0.00436 (33)	−0.00128 (22)
Cl(4)	0.0196 (10)	0.00611 (43)	0.00148 (12)	−0.00151 (56)	0.00148 (27)	0.00054 (19)
Cl(5)	0.0172 (10)	0.00766 (48)	0.00162 (13)	−0.00564 (56)	0.00170 (28)	−0.00140 (20)
Cl(6)	0.01359 (96)	0.01851 (96)	0.00238 (17)	0.00924 (81)	−0.00258 (31)	−0.00277 (32)
Cl(7)	0.00571 (61)	0.00642 (43)	0.00381 (19)	−0.00032 (43)	0.00099 (26)	−0.00079 (24)
Cl(8)	0.01283 (81)	0.00689 (44)	0.00185 (13)	−0.00376 (49)	0.00182 (26)	−0.00136 (19)
Cl(9)	0.01117 (79)	0.00709 (44)	0.00206 (14)	−0.00358 (48)	0.00035 (25)	0.00119 (20)
Cl(10)	0.00854 (68)	0.00903 (49)	0.00150 (12)	0.00139 (46)	0.00143 (22)	−0.00042 (20)
Cl(11)	0.01386 (92)	0.00415 (38)	0.00357 (19)	0.00005 (46)	0.00183 (33)	0.00121 (22)
Cl(12)	0.00910 (70)	0.00827 (47)	0.00178 (13)	0.00444 (48)	0.00071 (23)	0.00072 (20)
Cl(13)	0.01095 (75)	0.00458 (36)	0.00214 (13)	0.00162 (42)	0.00138 (24)	0.00124 (18)
Cl(14)	0.01362 (85)	0.00543 (39)	0.00170 (13)	0.00040 (46)	0.00070 (25)	−0.00120 (18)
Cl(15)	0.00559 (57)	0.00504 (35)	0.00296 (15)	0.00070 (37)	0.00126 (23)	0.00020 (19)
N(1)	0.0112 (23)	0.0040 (11)	0.0011 (3)	0.0003 (12)	0.0015 (7)	−0.0006 (5)
C(11)	0.0104 (28)	0.0045 (14)	0.0012 (4)	−0.0024 (16)	0.0003 (8)	0.0010 (7)
C(12)	0.0134 (36)	0.0125 (26)	0.0016 (6)	0.0059 (25)	0.0025 (11)	−0.0008 (9)
C(13)	0.0034 (23)	0.0118 (23)	0.0021 (6)	0.0028 (19)	0.0010 (9)	−0.0004 (9)
C(14)	0.0098 (31)	0.0052 (17)	0.0031 (7)	−0.0019 (19)	−0.0002 (12)	0.0006 (9)
N(2)	0.0109 (25)	0.0058 (14)	0.0025 (5)	−0.0016 (14)	0.0012 (9)	0.0000 (7)
C(21)	0.0179 (47)	0.0131 (29)	0.0031 (8)	0.0007 (31)	0.0027 (16)	−0.0034 (13)
C(22)	0.0372 (72)	0.0033 (18)	0.0042 (10)	0.0040 (27)	−0.0032 (21)	0.0013 (11)
C(23)	0.0141 (42)	0.0127 (29)	0.0054 (11)	−0.0060 (30)	0.0054 (18)	0.0014 (15)
C(24)	0.0110 (36)	0.0195 (37)	0.0024 (7)	0.0060 (32)	−0.0024 (12)	−0.0026 (13)
N(3)	0.0137 (28)	0.0075 (15)	0.0012 (4)	0.0017 (17)	0.0002 (8)	−0.0001 (6)
C(31)	0.0234 (58)	0.0072 (22)	0.0062 (13)	−0.0059 (29)	0.0076 (23)	−0.0004 (14)
C(32)	0.0071 (33)	0.0175 (36)	0.0038 (9)	0.0019 (29)	−0.0007 (13)	−0.0002 (15)
C(33)	0.0366 (80)	0.0048 (21)	0.0056 (13)	−0.0018 (31)	0.0048 (26)	−0.0034 (14)
C(34)	0.0290 (65)	0.0179 (39)	0.0019 (7)	−0.0092 (42)	0.0014 (17)	0.0011 (13)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}h1 + 2\beta_{23}kl)]$.

Table III. Intramolecular Distances in $[N(CH_3)_4]_3Pt(GeCl_3)_5$

Atoms	Distance, Å	Atoms	Distance, Å
Pt–Ge(1)	2.399 (3)	Ge(1)–Cl(1)	2.185 (7)
Pt–Ge(2)	2.424 (3)	Ge(1)–Cl(2)	2.210 (7)
Pt–Ge(3)	2.480 (3)	Ge(1)–Cl(3)	2.197 (7)
Pt–Ge(4)	2.410 (3)	Ge(2)–Cl(4)	2.193 (7)
Pt–Ge(5)	2.391 (3)	Ge(2)–Cl(5)	2.191 (7)
N(1)–C(11)	1.56 (3)	Ge(2)–Cl(6)	2.189 (8)
N(1)–C(12)	1.51 (3)	Ge(3)–Cl(7)	2.235 (7)
N(1)–C(13)	1.53 (3)	Ge(3)–Cl(8)	2.216 (7)
N(1)–C(14)	1.55 (3)	Ge(3)–Cl(9)	2.230 (7)
N(2)–C(21)	1.50 (3)	Ge(4)–Cl(10)	2.171 (6)
N(2)–C(22)	1.54 (3)	Ge(4)–Cl(11)	2.181 (7)
N(2)–C(23)	1.58 (3)	Ge(4)–Cl(12)	2.177 (7)
N(2)–C(24)	1.52 (3)	Ge(5)–Cl(13)	2.180 (6)
N(3)–C(31)	1.51 (3)	Ge(5)–Cl(14)	2.168 (7)
N(3)–C(32)	1.54 (3)	Ge(5)–Cl(15)	2.190 (6)
N(3)–C(33)	1.43 (3)		
N(3)–C(34)	1.55 (4)		

slit at a take-off angle of 1.0°, formed the basis for the least-squares refinement of cell parameters and orientation. This refinement was effected using the logic documented by Busing and Levy[6] in the PDP-8/L computer.

Intensity data were collected at a takeoff angle of 1.0°; at this angle the peak intensity for a typical strong reflection was about 85% of the maximum value as a function of takeoff angle. The counter aperture was 5.0 mm high by 5.0 mm wide and was positioned 32 cm from the crystal. The data were collected by the θ–2θ scan technique at a scan rate of 2°/min. Allowance was made for the presence of both $K\alpha_1$ and $K\alpha_2$ radiations, the scan range for each reflection being from 1.0° below the calculated $K\alpha_1$ peak position to 1.0° above the calculated $K\alpha_2$ position. Stationary-counter stationary-crystal background counts of 10 sec were taken at the end of each scan. The diffracted beam was filtered through a 0.0015-in. Nb foil. The pulse height analyzer was set for approximately a 90% window, centered on the Mo $K\alpha$ peak.

A unique data set having $2\theta < 42°$ was gathered. A total of 4952 independent intensities were recorded. The intensities of three standard reflections were measured after every 100 reflections and showed only the deviations from the mean predicted from counting statistics. There were very few data above background at values of $2\theta > 42°$.

Data processing was carried out as described by Corfield, *et al.*[8] After correction for background the intensities were assigned standard deviations according to the formula[9] $\sigma(I) = [C + 0.25(t_s/t_b)^2 \cdot (B_H + B_L) + (pI)^2]^{1/2}$ and the value of p was selected as 0.05. This term in the expression is used to prevent extremely high weight being given to very large reflections.[10] The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects and for absorption. The absorption coefficient for this compound for Mo $K\alpha$ radiation is 80.7 cm^{-1} and for the crystal used the transmission coefficients were in the range 0.442–0.690.[11] Of the 4952 independent reflections, 3150 were greater than three times their estimated standard deviations; only these data were used in the refinement of the structure.

Solution and Refinement

All least-squares refinements in this analysis were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$; the weights w were taken as $4F_o^2/\sigma^2(F_o)^2$. In all calculations of F_c the atomic scattering factors for Pt, Ge, Cl, and N were taken from Cromer and Waber,[12] and those for C were taken from the tabulation of Ibers.[13]

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(8) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(9) J. T. Veal and D. J. Hodgson, *Inorg. Chem.*, 11, 597 (1972).

(10) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, 26, 563 (1957).

(11) The programs used in this analysis included local modifications of Hamilton's GONO9 absorption correction program, Ibers' NUCLS least-squares program, Busing, Martin, and Levy's ORFFE function and error program, Johnson's ORTEP plotting program, and Robinson and Dellaca's Fourier program.

(12) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

The effects of anomalous dispersion were included in calculations of F_c,[14] the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulations of Cromer.[15]

The position of the Pt atom was determined from a three-dimensional Patterson function, and three cycles of least-squares refinement on this position using a fixed isotropic thermal parameter were run. The usual agreement factors, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and R_2 (or weighted R factor) $= (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, were 0.524 and 0.599, respectively.

The five Ge atoms, 15 Cl atoms, and three NC_4 groups were located in subsequent difference Fourier maps, and least-squares refinement of these atoms with isotropic thermal parameters yielded values of 0.081 and 0.104 for R_1 and R_2, respectively. Two cycles of least-squares refinement with anisotropic thermal parameters reduced R_1 and R_2 to 0.059 and 0.079. At this stage it was evident that the low-angle data were of much lower quality than the average of the data set; R_1 for the 57 data with $2\theta < 10°$ was 0.127. This effect has been observed elsewhere[16-18] and has been ascribed to faulty background estimation which can result when relatively large scans are used and niobium filters are employed.[18,19] Consequently, these 57 data were rejected from the set and two further cycles were run; the final values of R_1 and R_2 were 0.054 and 0.068, and the significant improvement in R_2 is taken as evidence that the decision to reject the low-order data was valid. A difference Fourier synthesis computed at this stage still showed two peaks higher than 2 e $Å^{-3}$, but they could not be interpreted on the basis of any reasonable geometry. Since these large peaks were in the vicinity of the Pt atom, they probably stem from an error in the absorption correction which could have resulted from incorrect measurement of the coated crystal. All attempts to locate the methyl hydrogen atoms proved unsuccessful.

In the last cycle of least squares, the largest shift experienced by any parameter was 0.2 times its estimated standard deviation, which is taken as evidence that the refinement had converged. The value of R_2 shows no dependence on $\sin\theta$ or on $|F_o|$, which suggests that our weighting scheme is appropriate. Examination of the final values of $|F_o|$ and $|F_c|$ suggests to us that no correction for secondary extinction is necessary. The positional and thermal parameters derived from this last least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A table of structure amplitudes is available.[20]

Description of the Structure

The structure consists of discrete $Pt(GeCl_3)_5{}^{3-}$ and $N(CH_3)_4{}^+$ ions. The geometry of the $Pt(GeCl_3)_5{}^{3-}$ anion is shown in the figure, and it is apparent that the coordination around the platinum is considerably distorted from trigonal-bipyramidal symmetry. The most severe angular distortion from idealized trigonal-bipyramidal geometry is the Ge(1)-Pt-Ge(2) angle of 141.46 (10)°. This distortion is not, however, sufficient to allow a description of the ion as a distorted tetragonal pyramid, in which case this angle would more nearly approach 180°. Moreover, the atoms Pt, Ge(1), Ge(2), and Ge(3) which form the trigonal plane in the trigonal-bipyramidal description are roughly coplanar, with no atom deviating from the least-squares plane by more than 0.004 Å, while the atoms Ge(1), Ge(2), Ge(4), and Ge(5) which would form the basal plane of a tetragonal pyramid deviate markedly from planarity, with Ge(4) and Ge(5) approximately 0.35 Å above the least-squares plane and Ge(1) and Ge(2) a similar distance below it. The geometry of $[Pt(GeCl_3)_5]^{3-}$, however, is different from that of $[Pt(SnCl_3)_5]^{3-}$ since the latter is reported to have nearly regular trigonal-bipyramidal geometry. The intramolecular distances and angles are given in Tables III and IV.

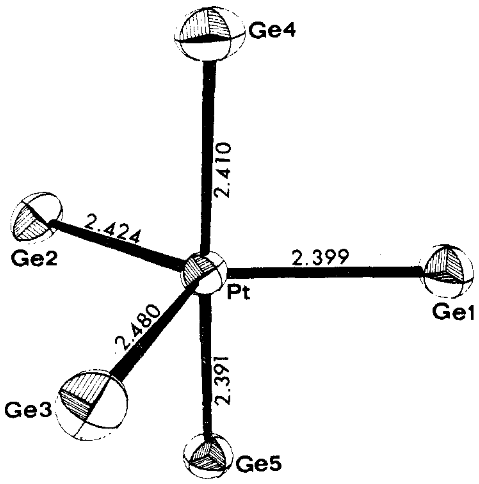

Figure 1. View of the $[Pt(GeCl_3)_5]^{3-}$ ion in $[N(CH_3)_4][Pt(GeCl_3)_5]$. The thermal ellipsoids are drawn at the 40% probability level.

Table IV. Intramolecular Angles in $[N(CH_3)_4]_3Pt(GeCl_3)_5$

Atoms	Angle, deg	Atoms	Angle, deg
Ge(1)-Pt-Ge(2)	141.5 (1)	Cl(10)-Ge(4)-Cl(11)	98.6 (3)
Ge(1)-Pt-Ge(3)	111.1 (1)	Cl(10)-Ge(4)-Cl(12)	99.5 (3)
Ge(2)-Pt-Ge(3)	107.5 (1)	Cl(11)-Ge(4)-Cl(12)	101.0 (3)
Ge(1)-Pt-Ge(4)	87.8 (1)	Pt-Ge(5)-Cl(13)	116.5 (2)
Ge(2)-Pt-Ge(4)	90.9 (1)	Pt-Ge(5)-Cl(14)	120.5 (2)
Ge(3)-Pt-Ge(4)	92.6 (1)	Pt-Ge(5)-Cl(15)	118.5 (2)
Ge(1)-Pt-Ge(5)	89.6 (1)	Cl(13)-Ge(5)-Cl(14)	97.3 (3)
Ge(2)-Pt-Ge(5)	89.0 (1)	Cl(13)-Ge(5)-Cl(15)	102.0 (3)
Ge(3)-Pt-Ge(5)	91.6 (1)	Cl(14)-Ge(5)-Cl(15)	98.0 (3)
Ge(4)-Pt-Ge(5)	175.7 (1)	C(11)-N(1)-C(12)	112 (2)
Pt-Ge(1)-Cl(1)	120.9 (2)	C(11)-N(1)-C(13)	108 (2)
Pt-Ge(1)-Cl(2)	116.0 (2)	C(11)-N(1)-C(14)	111 (2)
Pt-Ge(1)-Cl(3)	122.2 (2)	C(12)-N(1)-C(13)	108 (2)
Cl(1)-Ge(1)-Cl(2)	99.8 (3)	C(12)-N(1)-C(14)	110 (2)
Cl(1)-Ge(1)-Cl(3)	95.0 (3)	C(13)-N(1)-C(14)	109 (2)
Cl(1)-Ge(1)-Cl(3)	98.0 (3)	C(21)-N(2)-C(22)	112 (3)
Pt-Ge(2)-Cl(4)	116.0 (2)	C(21)-N(2)-C(23)	104 (2)
Pt-Ge(2)-Cl(5)	120.4 (2)	C(21)-N(2)-C(24)	115 (2)
Pt-Ge(2)-Cl(6)	124.0 (2)	C(22)-N(2)-C(23)	109 (3)
Cl(4)-Ge(2)-Cl(5)	97.2 (3)	C(22)-N(2)-C(24)	108 (3)
Cl(4)-Ge(2)-Cl(6)	98.2 (4)	C(23)-N(2)-C(24)	109 (2)
Cl(5)-Ge(2)-Cl(6)	95.5 (4)	C(31)-N(3)-C(32)	110 (3)
Pt-Ge(3)-Cl(7)	123.5 (2)	C(31)-N(3)-C(33)	110 (3)
Pt-Ge(3)-Cl(8)	118.9 (2)	C(31)-N(3)-C(34)	101 (3)
Pt-Ge(3)-Cl(9)	120.9 (2)	C(32)-N(3)-C(33)	116 (3)
Cl(7)-Ge(3)-Cl(8)	95.5 (3)	C(32)-N(3)-C(34)	109 (3)
Cl(7)-Ge(3)-Cl(9)	95.6 (3)	C(33)-N(3)-C(34)	109 (3)
Cl(8)-Ge(3)-Cl(9)	96.1 (3)		
Pt-Ge(4)-Cl(10)	116.7 (2)		
Pt-Ge(4)-Cl(11)	119.5 (2)		
Pt-Ge(4)-Cl(12)	117.9 (2)		

Four of the five Pt-Ge bond lengths lie in the range 2.391 (3)-2.424 (3) Å, with an average value of 2.406 (8) Å, while the fifth bond of 2.480 (3) Å is considerably longer (and, presumably, weaker) than these four. There is no apparent stereochemical reason for this lengthening of the Pt-Ge(3) bond. Thus, a calculation in which Ge(3) and its associated chlorine atoms were moved 0.07 Å closer to the platinum along the observed Pt-Ge(3) vector revealed no abnormal intramolecular contacts. These Pt-Ge distances can be compared with the Ru-Ge distances[21] of 2.477 and 2.478 Å in *cis*- and *trans*-$Ru(CO)_4(GeCl_3)_2$ and suggest that the bonding here

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may be stronger than in the ruthenium complex. Quantitative comparison between these distances and those reported for $[Pt(SnCl_3)_5]^{3-}$ is precluded by the unreliable nature of the bond lengths in the latter complex.

The geometry at germanium is considerably distorted from tetrahedral, with Pt-Ge-Cl angles in the range 116.0 (2)-124.0 (2)° (av 119.5°) while the Cl-Ge-Cl angles are in the range 95.0 (3)-102.0 (3)° (av 97.8°). This trend was also observed[21] in $Ru(CO)_4(GeCl_3)_2$. The Ge-Cl bond lengths are from 2.168 (7) to 2.235 (7) Å, with an average value of 2.194 Å, which are appreciably longer than the average (uncorrected for thermal motion) of 2.153 Å in *trans*-$Ru(CO)_4(GeCl_3)_2$ but are consistent with the reported sum of the covalent radii[22] of Ge and Cl. The coordination at the nitrogen in each of the cations is roughly tetrahedral, with C-N-C angles in the range 101 (3)-116 (3)° (av 109°). The C-N bond lengths are from 1.43 (3) to 1.58 (3) Å (av 1.53 Å).

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2932.

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Crystal and Molecular Structure of Dinitrato[2-(2-dimethylaminoethyl)pyridine]copper(II)

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The crystal and molecular structure of dinitrato[2-(2-dimethylaminoethyl)pyridine]copper(II), Cu(DMAEP)$(NO_3)_2$, has been determined from three-dimensional counter X-ray data. The material crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell and cell constants of $a = 6.688$ (6), $b = 14.310$ (11), $c = 14.285$ (9) Å, and $\beta = 78.46$ (3)°. The observed and calculated densities are 1.64 (3) and 1.675 g cm^{-3} and the structure was refined by full-matrix least-squares procedures to a final value of R of 0.037 for 1576 independent reflections having $F^2 > 3\sigma(F^2)$. The copper(II) ions are unsymmetrically coordinated to two bidentate nitrate groups and to the nitrogen atoms of the DMAEP ligand. The geometry at the copper(II) ion is distorted octahedral with elongated axial positions occupied by oxygen atoms from both nitrate groups with Cu-O bond distances of 2.468 (4) and 2.479 (4) Å. The equatorial plane bond distances are considerably shorter, with Cu-N bond lengths of 1.966 (4) and 2.014 (4) Å and Cu-O bond lengths of 1.990 (3) and 2.019 (4) Å.

Introduction

Complexes of the type $CuLX_2$ where L is a substituted 2-(2-aminoethyl)pyridine and X a halogen were first reported by Uhlig and coworkers,[1,2] who suggested that the complexes are dimeric with five-coordinate geometry at the copper atom. Recent reports of the structures of Cu(AEP)Br_2[3] and Cu(AEP)Cl_2,[4] where AEP is 2-(2-aminoethyl)pyridine, have shown these complexes to be polymeric with six-coordinate geometry at the copper atom and both polymeric chain and pairwise copper-halogen-copper linkages.

The ability of the pseudo-halogen, nitrate, to act as a ligand in transition metal complexes has been well documented during the past 15 years.[5] Like the halogens, the nitrate group has been shown to act as a monodentate ligand or as a bifunctional bridge in both dimeric and polymeric cases. In addition, nitrate frequently serves as either a symmetrically or unsymmetrically bidentate ligand occupying two coordination sites on the same metal center. In view of the known polymeric nature of Cu(AEP)Br_2 and Cu(AEP)Cl_2 and the coordinating versatility of the nitrate group, a number of molecular geometries can be postulated for a substituted 2-(2-aminoethyl)pyridinecopper(II) nitrate complex. In order to further our investigations into the geometries of copper(II) chelates and the coordination of the nitrate group we have undertaken the three-dimensional structural determination of dinitrato[2-(2-dimethylaminoethyl)pyridine]copper(II).

Data Collection and Reduction

The complex was prepared by addition of equimolar amounts of 2-(2-dimethylaminoethyl)pyridine (DMAEP) and $Cu(NO_3)_2 \cdot 3H_2O$ in acetone. After several hours deep blue crystals which were suitable for X-ray examination appeared. *Anal.* Calcd for $CuC_9N_4O_6H_{14}$: C, 32.00; N, 16.59; H, 4.19. Found: C, 32.01; N, 16.50; H, 4.16.

Preliminary Weissenberg and precession photographs indicated that the crystals belong to the monoclinic system. The systematic absences which were observed are $0k0$ for k odd and $h0l$ for l odd which indicates that the space group is $P2_1/c$. The cell constants obtained by the least-squares procedure of Busing and Levy[6] are $a = 6.688$ (6), $b = 14.310$ (11), $c = 14.285$ (9) Å, and $\beta = 78.46$ (3)°;

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