Inorganica Chimica Acta, 58 (1982) 227–231

Synthesis and Low-Frequency Vibrational Spectra of N-(2-Ammoniumethyl)-Piperazinium Halide-Mercurates(II). Crystal Structure of N-(2-Ammoniumethyl)-Piperazinium Monochloride Tetrachloromercurate(II)

LEDI MENABUE, GIAN CARLO PELLACANI

Istituto di Chimica Generale ed Inorganica, Università di Modena, Via Campi 183, 41100 Modena, Italy

ALBERTO ALBINATI, FABIO GANAZZOLI

Istituto di Chimica, Politecnico di Milano, Piazza L. da Vinci, e Istituto di Chimica Farmaceutica e Tossicologica dell'Università, 20133 Milan, Italy

FRANCO CARIATI and GLORIA RASSU

Istituto di Chimica Generale, Università di Sassari, Via Vienna 2, 07100 Sassari, Italy

Received June 6, 1981

Compounds of the type [N(2amet)pipzH_3]-[HgX_4] X (N(2amet)pipzH_3 = N-(2-ammoniumethyl)-piperazinium trication; X = Cl, Br) have been prepared and characterized by means of Raman and far-IR spectroscopy. The crystal determination of [N(2amet)pipzH_3][HgCl_4] Cl shows that it is composed of discrete monomeric [HgCl_4]$^{2-}$ units, chloride and [N(2amet)pipzH_3]$^{3+}$ ions. Co-ordination around the mercury atom is a distorted tetrahedron with two shorter and two longer Hg–Cl distances (av. 2.440(9) and av. 2.556(9) Å, respectively).

Introduction

The mercury(II) halides are rather interesting, showing a variety of co-ordination numbers and geometries [1, 2]. Although low-frequency vibrational spectroscopy has been widely used in their study, the relation between spectra and crystal structure is well defined for mercury(II) chloride and bromide [3] and for trichloro and tetrachloro mercury(II) complexes, only complexes which have polymeric structures containing [HgCl_6] octahedra [4]. The lack of this type of study for truly tetrahedral [HgCl_4] species probably derives from the fact that at present only for two compounds has the X-ray analysis evidenced the presence of these units [5, 6].

In the present work we have made a systematic investigation of the halomercurates(II) containing discrete monomeric [HgX_4] units in order to assign their low frequency vibrational spectra on the basis of their known structures, and to rationalize the conditions and forces which have a determining influence on the geometry of the halomercurates(II).

Experimental

The complexes having formulae [N(2amet)-pipzH_3] [HgX_4] X (where X = Cl, Br) were prepared by mixing ethanolic or methanolic solutions of mercury(II) halides and of the halide salts of N-(2-ammoniumethyl)-piperazinium trication in metal-to-ligand molar ratio 1:1, recrystallized from methanol. The compounds are white, crystalline solids, stable in the air and insoluble in non-polar organic solvents. Analytical data are in agreement with the cited formulae, within experimental error. Nitrogen, carbon and hydrogen were analysed with a Carlo Erba Elemental Analyser Instrument, Model 1104. The halogens were directly determined from aqueous solutions of the complexes by the Volhard method (Found: C, 14.17 H, 3.52; Cl, 34.70; N, 8.25; m.p. 228 °C. Calc. for $C_6H_{18}Cl_5N_3Hg$: C, 14.12; H, 3.55; Cl, 34.75; N, 8.23. Found: C, 9.83; H, 2.45; Br, 54.62; N, 5.75; m.p. 236 °C. Calc. for $C_6H_{18}Br_5N_3Hg$: C, 9.84; H, 2.47; Br, 54.55; N, 5.73).

Physical Measurements

Infrared spectra were recorded with a Perkin Elmer 180 spectrophotometer in nujol mull on polythene. Raman spectra were recorded with a Coderg PHO spectrophotometer equipped with krypton and argon lasers on solid samples.

Determination and Refinement of the Crystal Structure

Great difficulties were experienced in obtaining single crystals suitable for X-ray analysis. After recrystallization of the compounds the best crystals, although not completely satisfactory, were obtained for N-(2-ammoniumethyl)-piperazinium monochloride tetrachloromercurate(II). In all cases so far encountered by us [7] during the structural studies of $[Hg_xCl_y]^{n-}$ anions it has been extremely difficult to find single crystals of suitable quality, due to very high mosaic spread, structural disorder and twinning. A crystal of approximate dimensions 0.4 X 0.2 X 0.2 mm was used for the data collection. From the systematic absences the space group was established to be $P2_1/c$; the cell constants reported in the crystal data were determined from least-squares fit of the 2θ values of 25 general reflections ($2\theta \geq 20°$) measured on a Philips PW 1100 diffractometer which was subsequently used for the data collection.

Crystal Data

$C_6H_{18}Cl_5N_3Hg$; M = 510.1, monoclinic, a = 10.459(8), b = 10.875(8), c = 13.228(10) Å, β = 103.2(3)°, V = 1464 $Å^3$, Z = 4, D_{calc} = 2.31 Mg m^{-3}, λ(Mo Kα = 0.71096 Å), μ = (Mo Kα) = 113.9 cm^{-1}, space group $P2_1/c$. Intensities were collected using graphite monochromated Mo Kα radiation up to $2\theta \leq 46°$. An $\omega/2\theta$ scan technique was used with a scan speed of 0.05° s^{-1} and a scan width of 1.10°. Two background counts were measured at each side of the peaks for 10s and subsequently averaged. A total of 1781 independent reflections were measured, of which 1414 were considered as observed having $I \geqslant 3\sigma(I)$ (σ based on counting statistics) and used in the subsequent stages. During the data collection three standard reflections were measured every 90 min. to check the stability of the crystal and the experimental conditions. No significant variation of the intensities has been detected. Data have been corrected for Lorentz and polarization factors and an empirical absorption correction was applied using the ψ scan technique. The structure was solved by the heavy atom method and refined by full matrix and block diagonal least-squares, using anisotropic temperature factors for Hg and Cl atoms and isotropic factors for C and N. The final conventional agreement factor ($R = \Sigma(k|F_o| - |F_c|)/\Sigma k|F_o|$) is 0.095 for the observed reflections. The function minimised was $\Sigma w(k|F_o| - |F_c|)^2$ and the weighting factor was chosen after Cruickshank [8] as $w = 1/(c_1 + |F_o| + c_2|F_o|^2)$ with coefficients such that the function was approximately independent of $|F_o|$ and $\sin\theta/\lambda$. The contribution of hydrogen atoms, held fixed in the calculated positions (idealized geometry) was included in the last cycles of the least-squares refinement; the final difference map showed no significant features. Scattering factors were taken from Ref. [9]; the correction for the real part of the anomalous dispersion was taken into account for Hg and Cl atoms [9]. All calculations were carried out on an Univac 1100 computer using programs written by A. Immirzi [10]. The final atomic coordinates are given in Table I and a list of relevant bond lengths and angles is given in Table II.*

---

*A table of F_o/F_c may be obtained from the authors on request.

TABLE I. Final Positional and Thermal Parameters[a].

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg	0.1876(2)	0.1866(2)	0.1296(2)	2.7(1)	3.6(1)	3.0(1)	0.3(2)	5.2(2)	0.3(2)
Cl(1)	−0.0208(8)	0.2997(8)	0.1518(7)	2.2(4)	3.8(4)	3.6(4)	0.7(7)	5.0(7)	0.9(7)
Cl(2)	0.2382(9)	0.0702(9)	0.2919(7)	2.3(4)	3.9(4)	3.7(4)	−0.1(7)	4.4(7)	1.0(7)
Cl(3)	0.1749(10)	0.0856(10)	−0.0366(8)	4.5(5)	4.9(5)	3.5(5)	1.4(8)	4.6(8)	−1.3(8)
Cl(4)	0.3035(8)	0.3874(8)	0.1112(7)	3.2(5)	2.9(4)	4.7(5)	−0.7(7)	7.5(7)	−0.3(6)
Cl(5)	0.5861(9)	0.1234(8)	0.1680(7)	3.8(5)	3.1(4)	2.7(4)	0.2(7)	3.9(7)	−0.2(6)

	x/a	y/b	z/c	B(A^2)
C(1)	0.467(4)	0.318(4)	0.356(3)	3.7(7)
C(2)	0.617(4)	0.351(4)	0.361(3)	2.7(7)
C(3)	0.691(4)	0.178(3)	0.483(3)	2.5(6)
C(4)	0.545(4)	0.142(3)	0.479(3)	2.4(6)
C(5)	0.842(4)	0.261(4)	0.376(3)	2.8(7)
C(6)	0.924(4)	0.145(4)	0.381(3)	3.0(7)
N(1)	0.457(3)	0.254(3)	0.454(2)	2.0(5)
N(2)	0.696(3)	0.234(3)	0.379(2)	2.2(5)
N(3)	0.893(3)	0.072(3)	0.278(3)	3.2(6)

[a] The estimated standard deviations given in parentheses refer to the last significant figure. The anisotropic temperature factors are expressed as $T = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + B_{22}b^{*2}k^2 + B_{33}c^{*2}l^2 + 2B_{12}a^*b^*hk + 2B_{13}a^*c^*hl + 2B_{23}b^*c^*kl)]$.

TABLE II. Selected Interatomic Distances (Å) and Angles (°).[a]

Distances		Angles	
Hg–Cl(1)	2.577(9)	Cl(1)–Hg–Cl(2)	99.6(3)
Hg–Cl(2)	2.445(9)	Cl(1)–Hg–Cl(3)	116.4(3)
Hg–Cl(3)	2.434(9)	Cl(1)–Hg–Cl(4)	92.0(3)
Hg–Cl(4)	2.535(8)	Cl(2)–Hg–Cl(3)	121.0(3)
$(C–N)_{Av}$	1.52(5)	Cl(2)–Hg–Cl(4)	121.2(3)
$(C–C)_{Av}$	1.56(5)	Cl(3)–Hg–Cl(4)	103.4(3)
		$(C–N–C)_{Av}$	111.1(22)
		$(N–C–C)_{Av}$	110.3(24)

[a] The estimated standard deviations given in parentheses refer to the last significant figure.

Results and Discussion

Crystal Structure of [N(2amet)pipzH$_3$][HgCl$_4$]Cl

The crystal structure of the title compound is composed of discrete monomeric $[HgCl_4]^{2-}$ units, chloride and $[N(2amet)pipzH_3]^{3+}$ ions connected by a network of short hydrogen bonds. As shown in the perspective view of the molecule (Fig. 1) the mercury is co-ordinated by four chlorine atoms in a distorted tetrahedral arrangement, one of the two common co-ordination number for mercury(II) in the solid state [2].

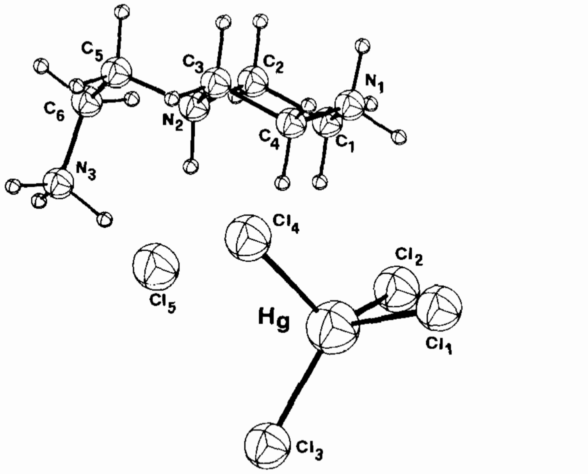

Fig. 1. Perspective view of the $[N(2amet)pipzH_3][HgCl_4]Cl$.

At present the tetrahedral $[HgCl_4]^{2-}$ ion has been found by X-ray structural determination only for the compounds $(SbzSbz)_2[HgCl_4]$ (SbzSbz = bis-(3,5-diphenyl-1,2-dithiolium) [5] and $[(CH_3)_4N]_2$-$[HgCl_4]$, the latter being isomorphous with the analogous bromo-derivative whose structure has been determined [6].

It has already been shown [1, 11] that long packing distances (comparable or shorter than the sum of Van der Waals radii) are important in determining the co-ordination number around the mercury atom and the relevant distortion from the idealized T_d geometry as found in this case. In fact there are two shorter distances Hg–Cl(2) and Hg–Cl(3) (av. value 2.440(9) Å) and two longer distances Hg–Cl(1) and Hg–Cl(4) (av. value 2.556(9) Å). The latter correspond to those chlorine atoms involved in hydrogen bond interactions (see later) with the NH group of the $[N(2amet)pipzH_3]^{3+}$ ion. Correspondingly Cl–Hg–Cl bond angles show large deviations from the ideal tetrahedral value being in the range 92.0–121.2° (av. value 108.9 ± 12.3; the ± sign referring to the mean square deviation), the smaller angle (Cl(1)–Hg–Cl(4), 92.0(3)°) being the one defined by the longer bonds. The average for the two short Hg–Cl bonds (2.440 ± 0.008 Å) may be compared with the value of 2.461(4) Å (average) found for similar bonds by Mason *et al.* [5] or the value of 2.40(2) Å found in $Hg_2Cl_5(NBzpipzH)$ [7].

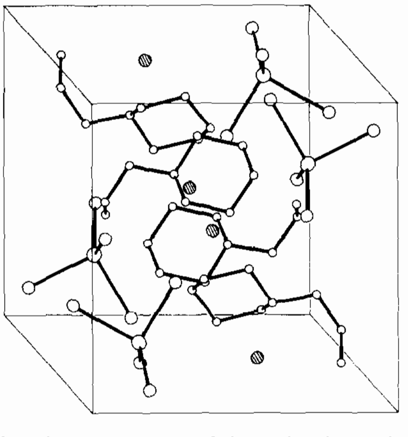

Fig. 2. Arrangement of the molecules in the unit cell.

On the other hand when chlorine atoms are part of a hydrogen bond network longer bonds are found, as for example in dichloro-bis-(O-ethylthiocarbamate)-mercury(II) [12] with a value of 2.58(1) Å. This value may be compared with the bond length of 2.556(9) Å of the present compound.

The packing distances may be subdivided into two sets. One contains the Cl–N or Cl–C distances (cfr. Table III) in the range 3.02–3.38 Å, shorter than the sum of Van der Waals radii (approximately 3.45 Å). Included in these distances are those between atoms Cl(1) and Cl(4) and the NH group and those between the chlorine ion Cl(5) and the ligand. Through the discussion a value of 1.75 Å for the Van der Waals radius of Cl^- has been used [13]. For the Hg(II) radius a revised value of 1.70 Å [14] has been chosen, longer than 1.50 Å as proposed by Grdenic [1]. The second set contains all the remaining distances greater than 3.40 Å, including inter alia those referring to atoms Cl(2) and Cl(3). The resulting packing is such that for the $[HgCl_4]^{2-}$ tetrahedron each of the two atoms Cl(1) and Cl(4) is

TABLE III. Some Significant Interaction Between Anions and Cations (Å).

Cl(1)–N(3)^{I}	3.23(5)	Cl(5)–N(1)^{IV}	3.14(3)
Cl(1)–N(3)^{II}	3.29(5)	Cl(5)–N(2)	3.02(4)
Cl(2)–N(1)	3.40(4)	Cl(5)–N(3)	3.26(4)
Cl(3)–N(1)^{IV}	3.46(4)	Cl(5)–C(2)	3.52(4)
Cl(3)–N(3)^{I}	3.55(4)	Cl(5)–C(3)^{IV}	2.61(5)
Cl(4)–N(1)^{IV}	3.28(3)	Cl(5)–C(4)^{IV}	3.53(5)
Cl(4)–C(1)	3.38(5)	Cl(5)–Hg	4.139(8)

Roman numerals superscripts refer to the following symmetry operations: I (x – 1, y, z); II (1 – x, $\frac{1}{2}$ + y, $\frac{1}{2}$ – z); III (1 – x, y, z); IV (x, $\frac{1}{2}$ – y, z – $\frac{1}{2}$).

involved in two short contacts with two different ligand molecules in the cell (see Table III), but there is no interaction between the mercury atom and the chloride ion Cl(5) (Hg–Cl(5), 4.139(8) Å.

The importance of the packing forces may also be inferred noting that the bromo compound with analogous stoichiometry is not isomorphous though the vibrational spectra (see later) are consistent with a distorted tetrahedral geometry for the $[HgBr_4]^{2-}$ moiety. It proved to be impossible to find crystals suitable for X-ray data collection for this compound. Preliminary crystal data have shown the crystals to be orthorhombic (a = 22.24(1), b = 11.88(1), c = 6.87(1); from systematic absences the space group is $P2_12_12_1$).

The $[N(2amet)pipzH_3]^{3+}$ ion is in a chair conformation (see Fig. 1). The average bond lengths for C–C is 1.56 ± 0.03 Å and for C–N 1.52 ± 0.04 Å. The average for the bond angles is 110.6°, a geometry comparable for example with that of piperidine hydrochloride [15].

Vibrational Spectra

As reported above, the mercury atom in $[N(2amet)pipzH_3][HgCl_4]Cl$ has a distorted tetrahedral co-ordination, the deviation from T_d symmetry being revealed both by the inequivalences in metal–chlorine distances and by the angular distortions (Cl–Hg–Cl) from the tetrahedral value. Consequently, more Hg–Cl stretching bands than those calculated for T_d symmetry should be expected in the Raman and IR spectra [16].

The far-IR and Raman spectra of this compound, together with those of $[N(2amet)pipzH_3]Cl_3$ for comparison, are shown in Figs. 3 and 4.

We have found for the Hg–Cl stretching vibrations one shoulder in the IR spectrum at 228 cm^{-1}, one strong band at 262 cm^{-1} and one weak band at about 220 cm^{-1} in the Raman spectrum. This is in agreement with what can be expected for a T_d symmetry of the $[HgCl_4]^{2-}$ anion [16]. The strong IR band is the F_2 asymmetric stretch while the strong Raman band is the A_1 symmetric stretch. The frequencies of these vibrations agree with those reported in the literature [17–19] for compounds containing the tetrahedral $[HgCl_4]^{2-}$ anion. Consequently the deviations from the perfect tetrahedral arrangement found in the present compound play no significant role in the vibrational spectra.

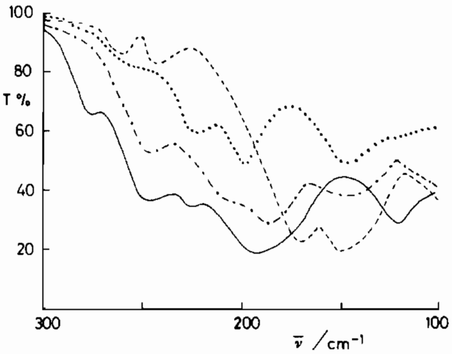

Fig. 3. IR spectra (nujol mulls) of $[N(2amet)pipzH_3][HgCl_4]Cl$ (———), $[N(2amet)pipzH_3][HgBr_4]Br$ (– – – –), $(N(2amet)pipzH_3)Cl_3$ (–•–•–•–), $(N(2amet)pipzH_3)Br_3$ (•••••).

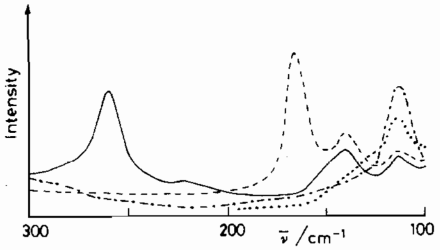

Fig. 4. Raman spectra of solid $[N(2amet)pipzH_3][HgCl_4]Cl$ (———), $[N(2amet)pipzH_3][HgBr_4]Br$ (– – – –), $(N(2amet)pipzH_3)Cl_3$ (–•–•–•–), $(N(2amet)pipzH_3)Br_3$ (•••••).

The Raman spectrum of the corresponding bromoderivative shows for the Hg–Br stretches a strong band at 168 cm^{-1} and a weak band at 142 cm^{-1}. It is worth noting that an analogous weak band is present in the Raman spectrum of the $[N(2amet)pipzH_3][HgCl_4]Cl$ (See Fig. 4).

The corresponding IR spectrum, reported in Fig. 3, shows two strong bands at 169 and 150 cm^{-1} assignable to the Hg–Br stretching vibrations. From these results we may suggest that in this compound the $[HgBr_4]^{2-}$ anion, having a distorted tetrahedral structure, is present because when it has T_d symmetry [6] both IR and Raman spectra show for the Hg–Br stretches only one strong band [17].

TABLE IV. Vibrational Stretching Frequencies (cm^{-1}) of $[HgX_4]^{2-}$ Anions with Tetrahedral Structure.[a]

Compound	$\nu(A_1)$		$\nu(F_2)$		Ref.
	Raman	IR	IR	Raman	
$[N(2amet)pipzH_3][HgCl_4]Cl$	262s	–	228sh	220vw	this work
$[N(2amet)pipzH_3][HgBr_4]Br$	168s	169s	150s, br	142w	this work
$(Me_4N)_2HgCl_4$	264m	–	225vs	230vw	19
$(Me_4N)_2HgBr_4$	164s	–	153vs	–	17
$(Et_4N)_2HgCl_4$	–	–	228s	–	18
$(Et_4N)_2HgCl_4$	268m	–	229vs	–	17
$(Et_4N)_2HgBr_4$	165s	–	154vs	–	17

[a] s = strong, m = medium, w = weak, v = very, sh = shoulder, br = broad.

We can reasonably assume that for this compound the splitting of the F_2 stretching frequency is low and that consequently the bands arising by the lowering of symmetry are included in the strong broad IR band at 150 cm^{-1} and in the corresponding weak Raman band at 142 cm^{-1}, the latter casually coincident with that found in the Raman spectrum of the analogous chloro-derivative and which could have another origin. Consequently the IR absorption at 169 cm^{-1} must be assigned to the Hg–Br total symmetric stretching vibration which by lowering of symmetry becomes IR active. The vibrational stretching frequencies attributed to the $[HgX_4]^{2-}$ (X = Cl, Br) groups, and their most probable assignments are reported in Table IV.

We believe that the degree of distortion from T_d symmetry of the $[HgX_4]^{2-}$ anions in the complexes studied could depend from the nature of the halogen atom. Unfortunately it was impossible to find crystals of $[N(2amet)pipzH_3][HgBr_4]Br$ suitable for an X-ray data collection. Consequently our hypothesis may not have been fully confirmed.

Acknowledgements

The authors are grateful to the Italian Consiglio Nazionale delle Ricerche (CNR) for financial support and the Centro Strumenti of the University of Modena for recording the IR spectra.

References

1 D. Grdenic, *Quart. Rev., 19,* 303 (1965).
2 P. A. W. Dean, *Progr. Inorg. Chem., 24,* 109 (1978).
3 D. M. Adams and D. J. Hills, *J. Chem. Soc. Dalton,* 776 (1978).
4 R. M. Barr and M. Goldstein, *J. Chem. Soc. Dalton,* 1180 (1974).
5 R. Mason, G. B. Robertson and G. A. Rusholm, *Acta Cryst., B30,* 894 (1974).
6 B. Kamenar and A. Nagl, *Acta Cryst., B32,* 1414 (1976).
7 A. Albinati, S. V. Meille, F. Cariati, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chim. Acta, 38,* 221 (1980).
8 D. W. J. Cruickshank in 'Crystallographic Computing', F. R. Ahmed Ed., Copenhagen Munksgaard, pp. 187–198 (1970).
9 'International Tables for X-Ray Crystallography', Kynoch Press, Birmingham, Vol. IV (1974).
10 A. Immirzi, *Ric. Sci., 37,* 743 (1967); *Ibid., J. App. Cryst., 6,* 246 (1973).
11 'Molecular Structure by Diffraction Methods', The Chem. Soc., London, Vol. 1–5 (1974–1978).
12 G. Bandoli, D. A. Clemente, L. Sindellari and E. Tondello, *J. Chem. Soc. Dalton,* 449 (1975).
13 A. Bondi, *J. Phys. Chem., 68,* 441 (1964).
14 A. J. Canty and G. B. Deacon, *Inorg. Chim. Acta, 45,* L225 (1980).
15 C. Rerat, *Acta Cryst., 13,* 72 (1960).
16 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Co-ordination Compounds', John Wiley and Sons, Inc., New York, (1978).
17 M. A. Hooper and D. W. James, *Aust. J. Chem., 24,* 1331 (1971).
18 D. M. Adams, J. Chatt, J. M. Davidson and J. Gerratt, *J. Chem. Soc.,* 2189 (1963).
19 G. B. Deacon, J. H. S. Green and W. Kynaston, *Aust. J. Chem., 19,* 1603 (1966).