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Infrared and polarized Raman spectra of $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$ single crystal

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Abstract

Infrared and polarized Raman spectra of $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$ single crystal have been recorded and analysed. The appearance of non-degenerate Se–OH stretching vibrations in the α_{xz} and α_{yz} polarizations of Raman spectra indicate distortion of the HSeO_3^- ion in the $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$ crystal. The low wavenumber values obtained for the symmetric and asymmetric stretching vibrations of the HSeO_3^- ion are consistent with the strong hydrogen bonding and the influence of Jahn–Teller distortion as predicted in X-ray diffraction data. The shifting of the stretching and bending vibrations of the hydroxyl groups and water molecules from the free state values also confirms the strong hydrogen bonding in this crystal. Broad bands observed for both stretching and bending regions become sharp in the Raman spectrum recorded at 77 K. A doublet appears for the Se–OH stretching mode at this temperature indicating the settling of protons in an ordered position and the absence of intrabond proton tunnelling.

1. Introduction

Divalent metals form hydrogen selenites $\text{M}(\text{HSeO}_3)_2$ and diselenites (MSe_2O_5) with selenious acid as well as normal selenites MSeO_3 [1]. Crystal structures of different selenites in the group, formed by divalent copper, have been reported [2–4]. Copper(II) hydrogen selenite monohydrate, $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$, shows a coordination octahedron with typical elongation of Cu–O bonds due to the Jahn–Teller effect [1]. In the present investigation IR and polarized Raman spectra of $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$ single crystal are studied to understand the physical properties of these crystals with particular emphasis on the behaviour of the protons engaged in hydrogen bonding.

2. Experimental

Transparent blue–green copper hydrogen selenite monohydrate (CHS) crystals were prepared by dissolving copper carbonate in a 1 mol dm^{-3} H_2SeO_3 solution, filtering the warm (40 °C) saturated solution and evaporating it at room temperature [1]. A spex 1401 double monochromator (slit widths 300–400 μm) equipped with a Spectra-Physics model 165 Ar^+ laser was used to record the Raman spectra in the Stokes region with an experimental resolution better than 3 cm^{-1} at room temperature ($300 \pm 3 \text{ K}$). Both 514.5 and 488.0 nm lines were used to record the spectra with a laser power of 100 mW. The

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crystallographic axes were determined using a polarizing microscope. A well polished crystal (4 mm × 2 mm × 1 mm) cut with sides parallel to the crystallographic axes was used for the polarized Raman studies in the $c(bb)a$, $c(ac)a$, $c(bc)a$ and $c(ab)a$ orientations. The crystal was oriented in a goniometer head and the measurements were taken at 90° scattering geometry. Raman spectrum of the crystal in the $c(bb)a$ orientation was also recorded in the internal mode region at liquid nitrogen temperature using a conventional liquid nitrogen cell. Infrared spectrum was recorded on a Perkin Elmer 577 spectrophotometer with the samples prepared as KBr pellets.

3. Factor group analysis

$\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$ crystallizes in the monoclinic system with space group $P2_1/c$ (C_{2h}^5) having two formula units in the crystallographic unit cell [1]. The hydrogen selenite ions in CHS have the shape of a trigonal pyramid with one Se–O bond stretched due to hydrogen atom bonded to this oxygen and they occupy general positions of the unit cell. The axial Cu–O bonds are longer than planar bonds and they are coordinated to water molecules (Fig. 1). The factor group analysis [5] predicts 81 normal modes, excluding acoustic modes and they split into

$$\Gamma_{\text{CHS}} = 20A_g + 20B_g + 21A_u + 20B_u$$

4. Results and discussion

4.1. HSeO_3 vibrations

A free selenite ion has C_{3v} symmetry with four distinct frequencies of vibrations: two associated with non-degenerate ν_1 and ν_2 modes and the other two with doubly degenerate ν_3 and ν_4 modes. If one hydrogen atom is attached to the selenite ion, its symmetry is lowered from C_{3v} to C_s and the degeneracy of the E modes is lifted [6] as given in Table 1.

The polarizability tensor components of ν_1 HSeO_3^- (C_s) are α_{xx} , α_{yy} , α_{zz} and α_{xy} (x , y and z corresponding to the a , b and c axes). In the factor group C_{2h} , they belong to the A_g species. Therefore, this mode will appear in all the orientations without any distortion of the HSeO_3^- ion. The ν_1 mode does not have α_{xz} and α_{yz} components in the C_s symmetry; but it can appear in the B_g orientation due to the distortion of the ion from C_s to C_1 , contributing to α_{xz} and α_{yz} components as seen in the spectra (Fig. 2). The appearance of ν_2 , ν_3 and ν_4 modes in both A_g and B_g species (Table 2) can also be

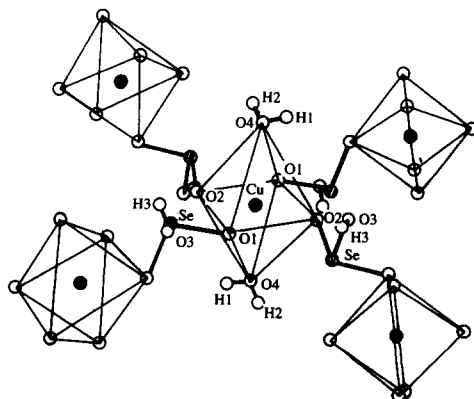


Fig. 1. A perspective view of the crystal structure of $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$ along the x -axis.

Table 1
Correlation scheme for the internal vibrations ^a of the SeO_3^{2-} ion in $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$

SeO_3^{2-} ion symmetry C_{3v}	HSeO_3^- ion symmetry C_s	Site symmetry C_1	Factor group symmetry $C_{2h}, Z^B = 2$
$\nu_1(A_1)\text{SeO}_3^{2-}$ [810] or $\nu_s(\text{Se-O})$	$\nu_3'(A')\text{HSeO}_3^-$ [845] or $\nu_s(\text{SeO}_2)$	A	$A_g + B_g + A_u + B_u$
$\nu_2(A_1)\text{SeO}_3^{2-}$ [425] or $\delta_s(\text{O-Se-O})$	$\nu_2(A')\text{HSeO}_3^-$ [468] or $\delta_s(\text{SeO}_2)$	A	$A_g + B_g + A_u + B_u$
$\nu_3(E)\text{SeO}_3^{2-}$ [740] or $\nu_{as}\text{Se-O}$	$\nu_1(A')\text{HSeO}_3^-$ [651] or $\nu(\text{Se-OH})$	A	$A_g + B_g + A_u + B_u$
	$\nu_3''(A'')\text{HSeO}_3^-$ [737] or $\nu_{as}(\text{SeO}_2)$	A	$A_g + B_g + A_u + B_u$
$\nu_4(E)\text{SeO}_3^{2-}$ [372] or $\delta_{as}(\text{O-Se-O})$	$\nu_4'(A')\text{HSeO}_3^-$ [328] or $\delta_s(\text{O-Se-OH})$	A	$A_g + B_g + A_u + B_u$
	$\nu_4''(A'')\text{HSeO}_3^-$ [355] or $\delta_{as}(\text{O-Se-OH})$	A	$A_g + B_g + A_u + B_u$

^a The frequencies (cm^{-1}) given in square brackets are from Ref. [10].

explained as due to this distortion-induced activity [7]. This is consistent with the low site symmetry (C_1) determined by the X-ray diffraction study.

The symmetric stretching vibrations of SeO_2 groups are expected at around 850 cm^{-1} (Table 1). Vibrational analysis on a series of alkali hydrogen selenites by Cody et al. and Micka et al., also shows that the symmetric stretching vibrations are around 850 cm^{-1} [8,9]. In the present study, the band corresponding to the symmetric stretching vibrations of SeO_2 groups is obtained at around 815 cm^{-1} in both A_g and B_g species of the Raman spectra (Fig. 2). A broad band of weak intensity is observed in the infrared spectrum for this mode.

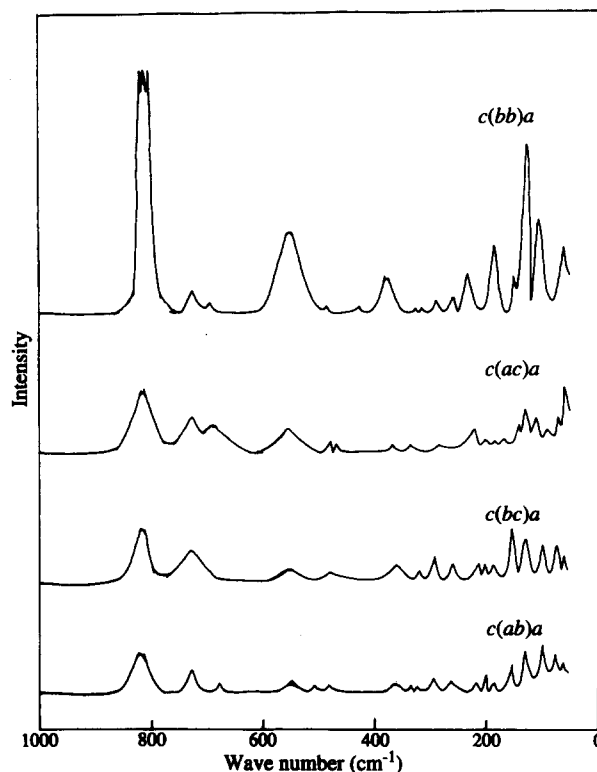


Fig. 2. Raman spectra of $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$ in the $50\text{--}1000\text{ cm}^{-1}$ region for $c(bb)a$, $c(ac)a$, $c(bc)a$ and $c(ab)a$ orientations.

Table 2
Spectral data (cm⁻¹) and band assignments of Cu(HSeO₃)₂ · H₂O

Raman					IR	Assignments
<i>c(bb)a</i> ^a	<i>c(bb)a</i>	<i>c(ab)a</i>	<i>c(ac)a</i>	<i>c(bc)a</i>		
	A _g	A _g	B _g	B _g		
	3478 w	3346 w	3390 wbr	3447 wbr	3460 mbr	
	3080 wbr	3146 vw	3067 wbr	3136 w	3148 sbr	ν ₃ , ν ₁ H ₂ O
					2840 sbr	ν _{OH(A)}
					2212 mbr	ν _{OH(B)}
					1785 mbr	ν _{OH(C)}
					1762 wbr	
	1664 wbr	1662 w	1654 wbr	1668 wbr	1641 mbr	ν ₂ H ₂ O
		1644 vw	1636 wbr	1624 vw		
					1280 wbr	δ _{OH}
818 m	815 vs	816 mbr	817 mbr	816 mbr	940–870 mbr	γ _{OH}
758 m					765 wbr	ν ₃ HSeO ₃ ⁻ or ν _s SeO ₂
732 m	725 mbr	725 mbr	728 mbr	730 mbr	728–679 sbr	ν ₃ HSeO ₃ ⁻ or ν _{as} SeO ₂
712 w						
699 wbr	688 wbr	682 wbr	686 mbr			
558 s	554 sbr	548 mbr	558 mbr	554 mbr	551 sbr	ν ₁ HSeO ₃ ⁻ or ν _{Se-OH}
548 m		508 vw				
484 w	483 w	482 w	480 w	488 w	449–408 mbr	ν ₂ HSeO ₃ ⁻ or δSeO ₂
441 w			472 w			
430 w	430 wbr					
380 m	379 mbr	360 mbr	364 vw	361 mbr	370 w	ν ₄ HSeO ₃ ⁻ or δ _{as} O–Se–OH
338 w	327 w	329 vw	338 w		328 mbr	ν ₄ HSeO ₃ ⁻ or δ _s O–Se–OH
318 vw	316 wbr	326 w		319 vw		
298 w	290 m	292 mbr	288 w	292 wbr	292 wbr	Cu–O stretching
267 w	260 mbr	262 mbr		262 wbr	251 vw	
					241 w	
226 s	223 mbr					
215 w		218 wbr	219 m	214 w	220 w	
		200 wbr	202 vw	203 w		
190 s	188 s	188 vw	186 vw	188 vw		External modes
			171 vw			
157 m	150 w	152 mbr	143 m	153 sbr		
138 vs	131 s	131 mbr	129 mbr	131 mbr		
108 w	106 m	98 s	113 mbr	98 mbr		
			93 w			
64 w	64 mbr	73 m	72 vw	73 m		
		64 w	62 s	61 w		

^a Spectrum recorded at liquid nitrogen temperature. Key: v, very; s, strong; m, medium; w, weak; br, broad, sh, shoulder.

The asymmetric stretching vibrations of SeO₂ groups are observed as medium intense bands in all the orientations. Corresponding IR spectrum gives an intense broad band in the 679–728 cm⁻¹ region. These modes are observed at lower wavenumbers than those in alkali hydrogen selenites [9].

The copper atoms are located at the centre of CuO₆ coordination octahedra. Four oxygen atoms from two didentately coordinated hydrogen selenite ions form a plane with Cu. The axial Cu–O bonds are longer and they are coordinated to water molecules. The high spin d-configuration of Cu leads to Jahn–Teller distortions to produce planar Cu–O bonds in the 1.927–1.986 Å range and an axial Cu–O distance of 2.574 Å. The fact that the planar oxygen atoms are shared by Cu and Se atoms can lead to the observed reduction in the stretching frequencies of the SeO₂ groups.

The stretching vibrations of the HSeO_3^- ion ($\nu_{\text{Se-OH}}$), usually observed in the 600–650 cm^{-1} region, are also obtained at lower wavenumbers ($\approx 555 \text{ cm}^{-1}$) in all the orientations. This mode is observed as an intense broad band at 551 cm^{-1} in the IR spectrum. The $\text{O} \cdots \text{O}$ distance involving the Se–OH system with one of the axial oxygen atoms of the neighbouring CuO_6 group is 2.662 Å. The observed lowering of the Se–O(H) vibrations from the free state values is confirmation of the corresponding strong hydrogen bonds predicted in the X-ray diffraction data [1].

Symmetric deformation vibrations of the HSeO_3^- ion (Table 2) give only weak bands in all orientations of the Raman spectra while a medium intense broad band is obtained in the IR. In the asymmetric bending vibration, Raman spectra show medium intense bands with a weak band in the IR. A reduction in the symmetry of the HSeO_3^- ion causes the changes in the activity of these modes.

It is to be noted that all bands, both stretching and bending, appear broad in both the IR and polarized Raman spectra. This is consistent with the strong hydrogen bonding and the distortion of CuO_6 octahedra due to the Jahn–Teller effect which also affect the HSeO_3^- vibrations.

Cody et al. [8] have attributed broad SeO_3^{2-} bands observed in any phase of the selenite salts to being an indication of rapid intrabond proton tunnelling, and this cannot be ruled out in this crystal. The Raman spectrum (50–1000 cm^{-1}) of CHS crystal in the $c(bb)a$ orientation recorded at liquid nitrogen temperature (77 K) shows that the intensity of the $\nu_s \text{SeO}_2$ vibrations is reduced considerably in the low temperature spectrum (Fig. 3). The Se–OH stretching vibrations become better resolved with intensity enhancement and an additional band appears at 548 cm^{-1} with medium intensity. The doublet bands arise from the inequivalence of the site of the molecules due to the reduction in symmetry [10–12] probably from the settling of a proton into an ordered position. This is further confirmed by the splitting of the bands observed in the SeO_2 asymmetric stretching region ($\nu_3 \text{HSeO}_3^-$) and the sharpening of all internal modes other than those observed in the room temperature spectrum [8]. From the above results, it can be inferred that the protons are more ordered in the low temperature phase with less probability of tunnelling [13,14]. In the lattice mode region also the bands become sharp and clearly resolved indicating that the translationally disordered vibrating groups become more ordered in the low temperature spectrum [15].

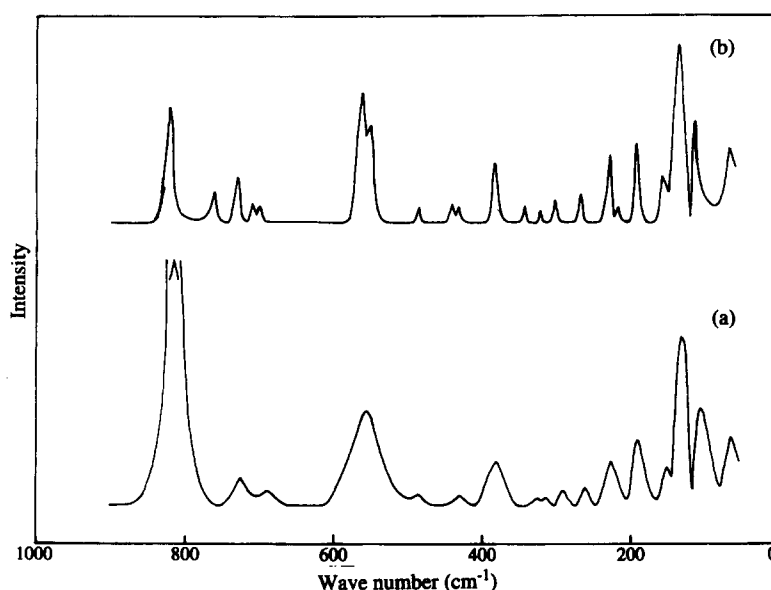


Fig. 3. Raman spectra of $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$: (a) at room temperature (303 K) and (b) at liquid nitrogen temperature (77 K), in the 50–1000 cm^{-1} region for the $c(bb)a$ orientation.

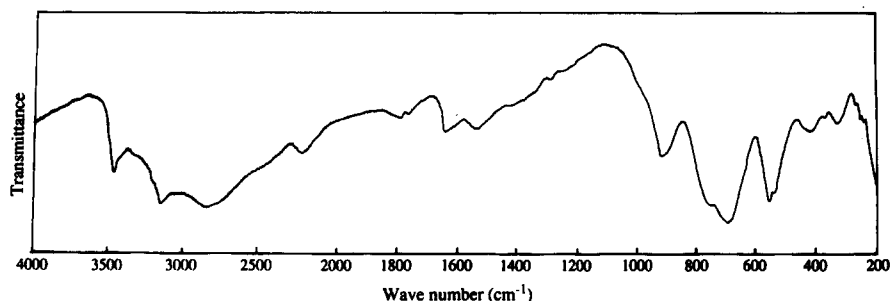


Fig. 4. Infrared spectrum of $\text{Cu}(\text{HSeO}_3)_2 \cdot \text{H}_2\text{O}$ in the $200\text{--}4000\text{ cm}^{-1}$ region.

4.2. Hydrogen bond/water vibrations

Hydrogen bonded OH groups lead to three fundamental vibrations, the $\nu(\text{OH})$ stretching and the in-plane $\delta(\text{OH})$ and the out-of-plane $\gamma(\text{OH})$ deformation vibrations. The stretching bands of strongly hydrogen bonded systems are very broad and are built up of a number of unresolved components due to strong interaction between the proton vibration and the $\nu(\text{O} \cdots \text{O})$ vibrations [16,17]. The broad $\nu(\text{OH})$ band in Fermi resonance with the overtones of the $\delta(\text{OH})$ the $\gamma(\text{OH})$ modes splits into three bands *A*, *B* and *C* [18,19]. The *A* mode is observed as a strong broad band at 2840 cm^{-1} in the IR spectrum while the *B* mode is obtained as a medium intense band at 2212 cm^{-1} . A medium intense broad band at 1785 cm^{-1} and a weak one at 1762 cm^{-1} are assigned to *C* bands (Fig. 4). The appearance of these bands confirms the existence of strong hydrogen bonds in the crystal.

The in-plane bending $\delta(\text{OH})$ vibrations are less sensitive to the hydrogen bond strength than the $\gamma(\text{OH})$ mode [20]. A weak band observed at 1280 cm^{-1} in the IR spectrum is attributed to the in-plane $\delta(\text{OH})$ bending mode and a medium intense broad band in the $870\text{--}940\text{ cm}^{-1}$ region to the $\gamma(\text{OH})$ mode.

Two broad bands are observed in the stretching region of water in the Raman spectra of CHS crystal. These bands are observed in all the polarization settings. In the IR spectrum, a strong broad band with two distinct peaks at 3460 and 3148 cm^{-1} are obtained for this mode. The bending mode of H_2O appears at around 1641 cm^{-1} in the IR. The considerable shifting of stretching and bending frequencies from those of a free water molecule [21] indicates the presence of strong hydrogen bonding in CHS crystal.

4.3. External modes

The external modes of the HSeO_3^- ion, lattice modes of water and metal–oxygen stretching modes appear below 300 cm^{-1} . Some of the Cu–O stretching vibrations are assigned in comparison with a normal coordinate calculation by Diaz [22].

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References

- [1] L. Hiltunen, M. Leskela, L. Niinisto and M. Tammenmaa, *Acta Chem. Scand. Ser. A*, 39 (1985) 809.
- [2] G. Gattow, *Acta Crystallogr.*, 11 (1958) 377.
- [3] K. Kohn, S. Akimoto, K. Inone, K. Asai and O. Horie, *J. Phys. Soc. Jpn.*, 38 (1975) 587.
- [4] G. Meunier, C. Svensson and A. Carpy, *Acta Crystallogr. Sect. B*, 32 (1976) 2664.

- [5] W.G. Fateley, F.R. Dollish, N.T. McDevitt and F.F. Bentley, *Infrared and Raman Selection Rules for Molecular and Lattice Vibrations — The Correlation Method*, Wiley, New York, 1972.
- [6] B.H. Torrie, *Can. J. Phys.*, 51 (1973) 610.
- [7] R. Bhattacharjee, *J. Raman Spectrosc.*, 21 (1991) 491.
- [8] C.A. Cody, R.C. Levitt, R.S. Viswanath and P.J. Miller, *J. Solid State Chem.*, 26 (1978) 281.
- [9] Z. Micka, M. Danek, J. Loub and B. Strauch, *J. Solid State Chem.*, 77 (1988) 306.
- [10] A. Sakai and I. Tatsuzaki, *J. Phys. Soc. Jpn.*, 50 (1981) 3016.
- [11] V.P. Dmitriev, L.M. Rabkin, V.I. Torgashev, L.A. Shuvalov and N.V. Gordeeva, *Sov. Phys. Crystallogr.*, 22 (1977) 186.
- [12] C.A. Cody, R.C. Levitt, R.K. Khanna and P.J. Miller, *J. Solid State Chem.*, 26 (1978) 293.
- [13] C.A. Cody and R.K. Khanna, *Indian J. Pure Appl. Phys.*, 16 (1978) 296.
- [14] L. Hiltunen, J. Holsa and Z. Micka, *J. Solid State Chem.*, 68 (1987) 307.
- [15] P.K. Khulbe, A. Agarwal, G.S. Raghuvanshi, H.D. Bist, H. Hashimoto, T. Kitagawa, T.S. Little and J.R. Durig, *J. Raman Spectrosc.*, 20 (1989) 283.
- [16] M.F. Claydon and N. Sheppard, *Chem. Phys.*, (1969) 1431.
- [17] S. Bartos and H. Ratajczak, *J. Mol. Struct.*, 76 (1982) 77.
- [18] J. Baran, T. Lis, M. Marchewka and H. Ratajczak, *J. Mol. Struct.*, 250 (1991) 13.
- [19] H. Ratajczak, A.M. Yaremko and J. Baran, *J. Mol. Struct.*, 275 (1992) 235.
- [20] J. Baran, Z. Czaplá and H. Ratajczak, *Acta Phys. Pol. A*, 70 (1986) 389.
- [21] S.N. Vinogradov and R.H. Linnel, *Hydrogen Bonding*, Van Nostrand Reinhold, New York, 1971.
- [22] G. Diaz, *Vib. Spectrosc.*, 6 (1993) 37.