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INFRARED SPECTROSCOPIC INVESTIGATION OF THE STRUCTURE OF SOME NATURAL ARSENATES AND THE NATURE OF H-BONDS IN THEIR STRUCTURES

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ABSTRACT

The IR-spectra of the arsenates durangite, mimetite, conichalcite, austinite, olivenite and adamite corroborate the character of the symmetry of the arsenate groups in these minerals. The changes in the symmetry of the point group of the anion $(AsO_4)^{3-}$ is the result of a coordinative bond with metal atoms. The hydroxyl group in conichalcite, austinite, olivenite and adamite is linked through H-bonds and coordinated with metal atoms. The frequencies of stretching vibrations of the hydroxyl group indicate that there are H-bonds with variable strengths between the OH groups and the oxygen in the O-AsO_3 groups. The strength of the H-bond falls in the following order: conichalcite > austinite > olivenite > adamite.

A band at 740 cm^{-1} in the spectra of Zn-bearing minerals such as adamite and austinite indicates that the oxygen atom of the arsenate group is partly protonated by the hydrogen atom of the OH group. This confirms that there is interaction between the anion and the cation (coordination) and that OAs (OH) groups may exist in the structure. The absence of bands in the 1500-1700 cm^{-1} region confirms the absence of water molecules in these minerals.

The following structural formulae are proposed: conichalcite, $Ca(CuOH)(AsO_4)$; austinite, $Ca(ZnOH)(AsO_4)$; olivenite, $Cu(CuOH)(AsO_4)$; and adamite, $Zn(ZnOH)(AsO_4)$.

INTRODUCTION

Durangite, $NaAl(AsO_4)F$, mimetite, $Pb_5(AsO_4)_3Cl$, adamite, $Zn_2(AsO_4)OH$, olivenite, $Cu_2(AsO_4)OH$, conichalcite, $CaCu(AsO_4)OH$ and austinite, $CaZn(AsO_4)OH$ have scarcely been studied by IR-spectroscopy. Adler (1961) and Moenke (1962) include the IR-spectra of some of these minerals, but they do not discuss them in detail and the spectra are used mainly for mineral identification. As *x*-ray data are available for this group of minerals, their IR-spectra, structures, and the nature of their chemical bonds may be correlated and analyzed.

All samples that were used were identified by optical methods and by *x*-ray analysis. The IR-spectra were registered with an IR-spectrophotometer (Zeiss, GDR) in the 400-3800 cm^{-1} region. The samples were prepared as emulsions in nujol. The spectra recorded were reproducible to ± 2 cm^{-1} in the 400-2000 cm^{-1} region and to ± 5 cm^{-1} in the 2000-3800 cm^{-1} region. Deuteration of the samples was carried out by means of a hermetic oven (Nasedkin 1962). Of the minerals studied, the only one completely deuterated was conichalcite and the substitution took about 20 hours.

All the minerals investigated are of the isolated tetrahedron type. Two, durangite and mimetite, have almost regular tetrahedrons and lack hydroxyl groups; the others (conichalcite, austinite, olivenite, and adamite) possess hydroxyl groups and their tetrahedral $(AsO_4)^{3-}$ structure is somewhat deformed. In the minerals investigated, three kinds of interactions are expected: 1) donor-acceptor, 2) H-bond and 3) electrostatic. The strongest type of interaction is probably the the donor-acceptor one, because most of the metallic cations are capable of forming strong complexes and because the anions are strong electrodonors. These interactions result in changes in the structure and in the chemical bonds and consequently the IR-spectra of these minerals are different from the spectra of free arsenates and free OH groups.

According to Mayantz (1960) and Siebert (1953, 1954, 1966), the tetrahedral symmetry, T_d, of the arsenate ion is indicated by four absorption bands of which only two appear in the IR-spectra and have the theoretical values $\nu_3(F_2) = 887$ cm^{-1} and $\nu_4(F_2) = 463$ cm^{-1}. The four bands appear in Raman spectra (Gupta 1948). When coordination of the arsenate ion with metals occurs, as in donor-acceptor bonds, then the symmetry of the arsenate group falls from $C_s(C_{3v})$ to C_{2v} (Fig. 1). A redistribution

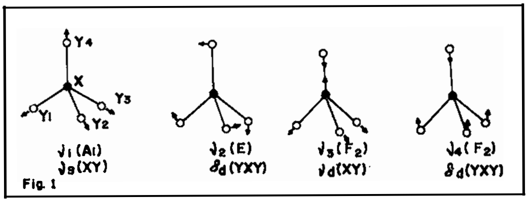

FIG. 1. Forms of vibration for the $(AsO_4)^{3-}$ tetrahedral group.

of the electronic cloud occurs which raises the strength of some of the As-O bonds, and decreases the strength of other bonds. This also results in the formation of new metal-oxygen bonds. The IR-spectra permit us to follow these changes and to interpret their nature. All the symmetry bands $\nu_1(A_1)$ and $\nu_2(E)$ are present. As the degeneracy of the $\nu_3(F_2)$ and $\nu_4(F_2)$ bands disappears, these split into two or three components and the band of valency vibrations of the *Me*-O(*Me* = metal) bond appears. Other bands related to the metal-arsenate system also appear. The coordination of the hydroxyl groups causes sharp changes in the IR-spectra. New bands related to deformation vibrations of the *Me*-OH bands appear in the 600-1200 cm^{-1} region and bands related to stretching vibrations appear in the 300-900 cm^{-1} region (Youxnevitch 1963, 1970).

MIMETITE

Mimetite, $Pb_5(AsO_4)_3Cl$, is an analogue of apatite and is hexagonal, bipyramidal, $6/m$. The unit cell has two $Pb_5(AsO_4)_3Cl$ units (Hendricks 1932; Machatski 1950). The As forms a regular tetrahedron with four oxygen atoms, in which the As-O distance is 1.82Å. The tetrahedra are interlinked by Pb atoms. The Pb atoms in the octahedra resemble empty cylinders on the walls of which are the Pb atoms, parallel to the *c* axis; the Cl atoms are distributed directly on the *c* axis. Pb forms a continuous column in which each Pb atom coordinates with 9 oxygens. These columns are linked together by the $(AsO_4)^{3-}$ tetrahedra.

We studied two samples of mimetite, one from Tsumeb, S.W. Africa, with 1.93% P_2O_5 and another from Cumberland, England, with 11% P_2O_5. The IR-spectra of both samples (Fig. 2) show a slight splitting in the region of stretching vibrations of the AsO_4 groups, that is, the $\nu_3(F_2)$ band. This splitting gives rise to two bands at 790 cm^{-1} and 820 cm^{-1}. The $\nu_1(A_1)$ band appears as a weak shoulder at 735 cm^{-1}. In the region of deformation vibrations of the arsenate ion there is a weak splitting of the $\nu_4(F_2)$ band into two bands at 415 cm^{-1} and 430 cm^{-1}. From the IR-spectral data we conclude that there is a slight deformation of the $(AsO_4)^{3-}$ tetrahedron, giving this mineral a C_{3v} symmetry. This agrees with the correlation scheme (Table 1) and with the *x*-ray data. The arrangement in the correlation table enables one to find the symmetry of the ligand in the structure of the minerals (Nakamoto 1966). The interatomic distances are Pb-Cl = 3.16Å and Pb-O = 2.56Å, which are bigger than the sums of the ionic radii (2.65Å and 2.16Å), and this fact indicates that the Pb-O bond is mainly ionic. The ionic nature of the Pb-O and Pb-Cl bands is also confirmed by the absence of absorption bands in the 500-600 cm^{-1} region where the bands of stretching vibrations of the *Me*-O bonds usually appear.

The IR-spectra of mimetite from Tsumeb, which has only traces of phosphate, show four bands of medium intensity in the region of valency vibrations of the phosphate group, that is in the $\nu_3(F_2)$ region. These bands are $\nu_{3a} = 960$ cm^{-1}, $\nu_{3b} = 990$ cm^{-1}, $\nu_{3c} = 1010$ cm^{-1} and a weak band $\nu_1(A_1) = 925$ cm^{-1} (Table 2). In the region of deformational vibrations, the $\nu_4(F_2)$ band is split in three bands: $\nu = 545$ cm^{-1}, $\nu_{4b} = 555$ cm^{-1} and $\nu_{4c} = 570$ cm^{-1}. This kind of splitting indicates that the site-symmetry of the $(PO_4)^{3-}$ group in the correlation scheme must correspond to C_{2v} symmetry, that is, to a symmetry lower than that of the $(AsO_4)^{3-}$ groups.

The IR-spectra of mimetite from Cumberland show an intense band $\nu_3(F_2)$ due to the phosphate anion. A weak band at 1320 cm^{-1} is probably due to an overtone 2 $\nu_4(PO_4)^{3-}$ and

TABLE 1. CORRELATION TABLE FOR GROUPS OF LOCAL SYMMETRY IN TETRAHEDRAL ANIONS (Nakamoto 1966)

		ν_1	ν_2	ν_3	ν_4
Td	infrared	-	-	F_2	F_2
	Raman spectra	A_1	E	F_2	F_2
C_{3v}	infrared	A_1	E	A_1+E	A_1+E
	Raman spectra	A_1	E	A_1+E	A_1+E
C_{2v}	infrared	A_1	A_1	$A_1+B_1+B_2$	$A_1+B_1+B_2$
	Raman spectra	A_1	A_1+A_2	$A_1+B_1+B_2$	$A_1+B_1+B_2$

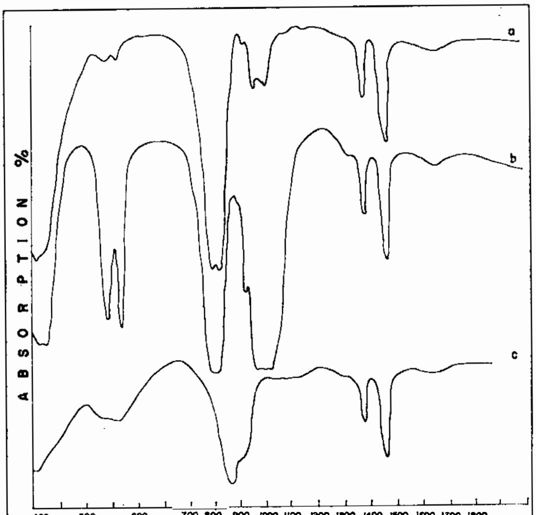

FIG. 2

FIG. 2. Infrared spectra of mimetite and durangite: (a) mimetite from Cumberland, England; (c) durangite from Durango, Mexico.

the 1650 cm^{-1} band may be related to the overtone 2 $\nu(AsO_4)^{3-}$.

Durangite

Durangite, $NaAl(AsO_4)F$, is a rare mineral. Its structure (Kokkoros 1938) is monoclinic, $2/m$, space group C_{2h}, $Z = 4$. The coordination number for Na is 7 and for Al, 6. The structure is of a sublayer type and is analogous to those of titanite and tilasite (Strunz 1938). In durangite, As forms a practically regular tetrahedron with As-O = 1.68Å in the $(AsO_4)^{3-}$ anion. The atoms of Al are surrounded by four oxygen atoms and by two F atoms that form an octahedral structure, AlO_4F_2, in which the interatomic distances are: Al-O = 1.81-1.90Å and Al-F = 1.81Å. In the vicinity of the Na atoms there are six O atoms and an F atom, with interatomic distances: Na-O = 2.40-2.47Å and Na-F = 2.35Å. These form NaO_6F polyhedra.

A fundamental difference between mimetite and durangite is the presence of Al atoms in durangite that are capable of forming strong covalent bonds. This is corroborated by the fact that the Al-O interatomic distances (1.81-1.90Å) are significantly lower than sum of the ionic radii (1.93Å). The coordination of the Al atoms with the arsenate groups in the structure of durangite decreases the As-O interatomic distance to 1.68Å as compared 1.82Å in mimetite, thus indicating that the As-O bond in durangite is the stronger.

The change in the energy of the valency bonds leads to changes in the IR-spectra. The frequencies of the As-O vibrations are 100 cm^{-1} higher than in mimetite (Table 2). The IR-spectra of durangite are considerably more complex than the spectra of mimetite (Fig. 2). In the region of valency frequencies $\nu_3(F_2)$, a very weak splitting is observed and it gives the bands ν_{3a} = 860 cm^{-1} and ν_{3b} = 915 cm^{-1}. In the $\nu_1(A_1)$ region there is a shoulder at 790 cm^{-1}. In the $\nu_4(F_2)$ region that corresponds to deformation vibrations, two bands are observed: ν_{4a} = 415 cm^{-1} and ν_{4b} = 450 cm^{-1}. This kind of splitting clearly points to a deformation in the $(AsO_4)^{3-}$ groups giving a C symmetry, which is in agreement with the correlation table and the x-ray data of Kokkoros (1938).

The IR-spectra of mimetite, which is a typical ionic compound, clearly differ from the spectra of durangite, which is a mineral with coordination bonds. For durangite, the two bands at 525 cm^{-1} and 560 cm^{-1} are probably due to antisymmetrical stretching vibrations of the Al-F and Al-O bonds in the octahedra. These two values are in the region of vibrational frequencies for the AlO_6 group (Nakamoto 1966). The observed spectral splitting may be explained as the result of a slight deformation in the symmetry of the octahedra. In durangite the 1030 cm^{-1} and 1098 cm^{-1} bands are probably due to the 2νAl-F and 2νAl-O overtones, and the 1650 cm^{-1} band is also probably due to an overtone $2\nu_3(AsO_4)^{3-}$.

It is concluded that the increase of the $\nu_3(F_2)$ value by 100 cm^{-1} and the appearance of a 560 cm^{-1} band related to Al-O bonds are a characteristic of coordination between arsenate groups and Al atoms. Therefore, it is possible to classify durangite as a compound with strong

TABLE 2. INFRARED ABSORPTION BAND FREQUENCIES.

	$[As(P)O_4]^{3-}$						Me-O	OH		OH..O	Overtone	
Mineral	$\nu_1(A_1)$		$\nu_3(F_2)$		$\nu_4(F_2)$							
	As-O	P-O	As-O	P-O	As-O	P-O	ν(Me-O)	δOH	νOH	ν(OH..O)	2ν	cm^{-1}
Mimetite $Pb_5[AsO_4]_3Cl$		925	790 820	960 990 1010	415 430	545 555 570					$2\nu_4(PO_4)^-$ $2\nu_3(AsO_4)^-$	1320 1650
Durangite $NaAl[AsO_4]F$			830* 860 915*		415 450		525(Al-F) 560				2ν(Al-F) 2ν(Al-O) $2\nu_3(AsO_4)$	1030 1098 1650
Olivenite $Cu_2[AsO_4]OH$	750*		800 830 870	1040 1090	400 452 492		545	950	3440	3050		
Adamite $Zn_2[AsO_4]OH$	740		800 830 860		400 485		515 535	900	3580	2900		
Conichalcite $CaCu[AsO_4]OH$	740*		795 820 840 865		410 430 460		575	930 1020 1060 (815)	3480 (2600) 3170 (2360) 2380	2090 2700 2730	$2\nu(AsO_4)$	1650
Austinite $CaZn[AsO_4]OH$	750		800 845		410 430 465		525 570	915 980 1010	3550 3300	1940 2450		

* shoulder ( ) frequencies of absorption bands of deuterated samples

covalent bonds and mimetite as a compound with bonds of an ionic nature.

CONICHALCITE AND AUSTINITE

The structure of austinite is not known, but as austinite and conichalcite are isomorphous, their structures must be of the same type. Both minerals are basic arsenates with isolated $(AsO_4)^{3-}$ groups in their structures. Their unit cell is orthorhombic with $4[CaCu(AsO_4)OH]$ in conichalcite and $4[CaZn(AsO_4)OH]$ in austinite. The conichalcite structure has been investigated by Strunz (1939) and Qurashi *et al.* (1953, 1954, 1963). The lattice of these two minerals consists of deformed $(AsO_4)^{3-}$ tetrahedra. Each Cu (or Zn) atom is surrounded by an octahedron of oxygen atoms, two of which belong to -OH groups and four to the arsenate group. Each Ca atom has eight neighbouring atoms. Seven are oxygen atoms belonging to arsenate groups and the eighth is an oxygen atom or a hydroxyl group. The interatomic distances are given in Table 3.

The sample of conichalcite that we used is from the Lachin-Han deposits, Uzbekhistan, and was provided by the Mineralogical Museum of the Academy of Sciences of the USSR (No. 64923). The Lachin-Han deposits and conichalcite have been thoroughly described by Dunin (1962).

The IR-spectra of conichalcite (Fig. 3a, Table 2) show a band splitting in the $\nu_3(F_2)$ region of vibrational frequencies of arsenate groups. The splitting gives four bands: $\nu_{3a} = 795$ cm^{-1}, $\nu_{3b} = 820$ cm^{-1}, $\nu_{3c} = 840$ cm^{-1}, and $\nu_{3d} = 865$ cm^{-1}. The $\nu_1(A_1)$ band is observed as a weak shoulder at 740 cm^{-1}. The region of deformation vibrations, $\nu_4(F_2)$, has three well-resolved bands $\nu_{4a} = 410$ cm^{-1}, $\nu_{4b} = 430$ cm^{-1}, and $\nu_{4c} = 460$ cm^{-1}. According to the correlation table (Table 1), the arsenate anion has a C_{2v} symmetry, which agrees with the *x*-ray data

TABLE 3. X-RAY DATA OF SOME ARSENATES WITH ISOLATED TETRAHEDRA IN THEIR STRUCTURES

Mineral	Ion	$O_{(1)}$	$O_{(2)}$	$O_{(3)}$	$O_{(4)}$	$O_{(5)}$/OH	Symmetry
Conichalcite $CaCu[AsO_4]OH$	As	1.74	1.67	1.73	1.60		
	Cu	2.09		2.38	2.28	1.95	
		2.04				1.95	
	Ca	2.54	2.68	2.53	2.51	2.36	
			2.48	2.46	2.54		
	OH	2.74		2.96			
		2.90		3.18	2.97		
		2.97			3.04		
Olivenite $Cu_2[AsO_4]OH$	As	1.49	1.45	1.81	1.81		
	$Cu_{(1)}$	2.12		2.34	2.34	1.96	
						1.96	
	$Cu_{(2)}$		2.03			1.99	
			2.16	1.92	1.92		
	OH	2.97	2.78	2.85	2.85		
Adamite $Zn_2[AsO_4]OH$	As	1.59	1.59	1.81	1.81	3.01	Deformed tetrahedron
	$Zn_{(1)}$	1.99		1.84	1.84	1.91	Trigonal bipyramid
		2.19					
	$Zn_{(2)}$		2.08	2.29	2.29	2.08	
			2.08			2.08	
	OH	2.68	3.03	2.79	3.04	2.86	

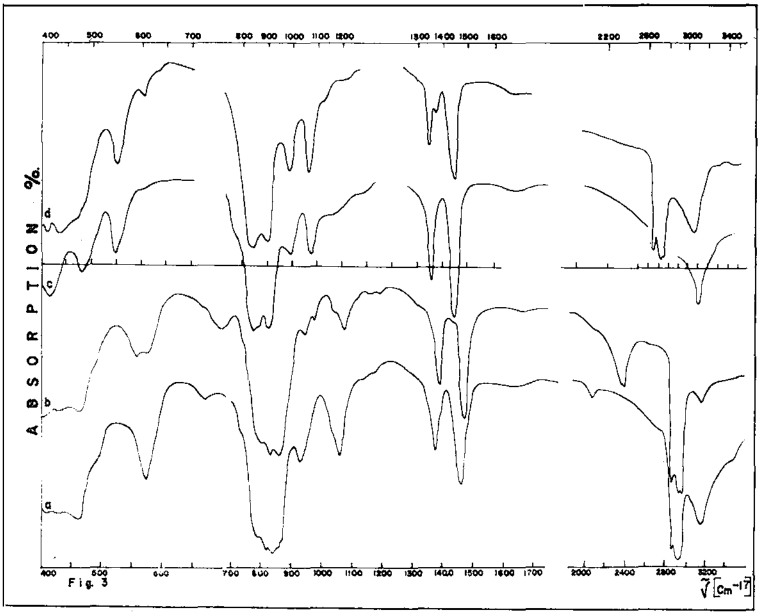

FIG. 3. Infrared spectra of conichalcite and austinite: (a) conichalcite from Lachin-han, USSR; (b) deuterated conichalcite from Lachin-han; (c) austinite from Hovon-aksi, USSR; (d) austinite from Ojue'a, Mexico. For cm^{-17} read cm^{-1}.

(Qurashi *et al.* 1963). A band of high intensity at 575 cm^{-1} is attributed to the stretching vibrations of the Cu-O bonds because the band does not change after deuteration of the mineral. The presence of Cu-O bonds is corroborated by *x*-ray data on the coordination of arsenate groups with Cu atoms. The interatomic distances of 2.04-2.28Å for the Cu-O bond are significantly less than the sum of the ionic radii, which is about 2.34Å (Qurashi *et al.* 1963). The 3480 cm^{-1} band is due to vibrations of the hydroxyl groups, which also give absorption bands at 3170 cm^{-1}, 1060 cm^{-1}, and 930 cm^{-1}. The relation of these bands with the hydroxyl groups is based on their shift after deuteration with D_2O (Fig. 3b). The spectra of deuterated conichalcite has the following features:

1. The 3170 cm^{-1} band is displaced to a lower frequency region and appears as two sharp, strong bands at 2360 cm^{-1} and 2380 cm^{-1}. The coefficient of isotopical shift is given by: OH 3170/OD 2370 ≃ 1.33.
2. The intensity of the 930 cm^{-1} band is lowered and the band shifts to a lower frequency (695 cm^{-1}). The shift also reveals a previously hidden band at 960 cm^{-1}. The coefficient of isotopical shift is given by: νOH 930/νOD 695 ≃ 1.33
3. The intensity of the 1060 cm^{-1} band is also lowered and its displacement reveals another band at 1020 cm^{-1}. Taking into consideration the coefficient of isotopical shift, the 1060 cm^{-1} band should be displaced to 750 cm^{-1}. Observation of the displaced band is obscured in this region by the stretching vibrations band $\nu_1(A_1)$ of arsenate groups.
4. The 3480 cm^{-1} band is probably shifted to 2600 cm^{-1} where a wide absorption band appears in the spectra of the deuterated samples.

The 3170 cm^{-1} band in the IR-spectra of conichalcite is related to the stretching vibrations of the OH groups in arsenates. These hydroxyl groups are linked, through strong H-bonds, with the oxygen of arsenate groups. In fact the oxygen atoms of the arsenate groups the strongest acceptors for H-bonds in the mineral. The *x*-ray data (Qurashi *et al.* 1963) show that the lowest value for the $O_{(5)} \ldots (HO)$ distance is 2.74Å, in agreement with the interatomic distance in a strong H-bond. The wide band at 3480 cm^{-1} is probably due to weaker H-bonds as is indicated by the higher interatomic distances (2.90-296Å) between oxygen atoms.

Two samples of austinite were used, one from Mapimi, Mexico and the other from Hovon-aski, Touva, USSR. The latter contains Mg (2.5%), Mn (1.6%) and Co and Ni (less than 1%) (Yahontova 1968). The Mapimi austinite has not been chemically analyzed.

The IR-spectra of both samples are very similar. In the $\nu_3(F_2)$ region, two bands were observed at 845 cm^{-1} and 800 cm^{-1}. The $\nu_1(A_1)$ band is poorly resolved and appears as a shoulder at 750 cm^{-1}. In the $\nu_4(F_2)$ region bands appear at 410 cm^{-1}, 430 cm^{-1} and a sharp shoulder at 465 cm^{-1}. This splitting (Fig. 3), according to the correlation table (Table 1), is probably linked to the site-symmetry of the arsenate ion. The arsenate group in austinite is probably less deformed than in conichalcite. This may be due to the specific crystallochemical properties of Zn that takes, in austinite, the place that Cu has in conichalcite.

The 525 cm^{-1} band is related to stretching vibrations of the Zn-O bonds. The Mapimi austinite shows a weak band at 570 cm^{-1} which is analogous to the band of stretching vibrations of Cu-O bonds in conichalcite; this band is probably due to the presence of traces of Cu in the austinite from Mapimi. The 915 cm^{-1} and 980 cm^{-1} bands are due to deformation vibrations *Me*O-H.

In the spectra of samples from Hovon-aksi (Fig. 3c), the region of valency vibrations of OH groups shows a sharp symmetrical band at 3300 cm^{-1} and a poorly-resolved wide band which appears as a shoulder at 3350 cm^{-1}. The IR-spectra of austinite from Mapimi show an asymmetrical band at 3270 cm^{-1} and a shoulder at 3520 cm^{-1}, which are due to the presence of H-bonds of different strength. This difference in strength of the H-bonds is probably linked to differences in the cationic composition of the two samples. (The 1400 cm^{-1} band in the IR-spectra of austinite from Mapimi indicates the presence of carbonate that is probably a mechanical contamination).

As the frequencies of the stretching vibrations of the hydroxyl groups in conichalcite (3170 cm^{-1}) are lower than in austinite (3270 cm^{-1} and 3300 cm^{-1}), the H-bonds are stronger and shorter in conichalcite than in austinite. From the comparison of IR-spectra and *x*-ray data the arsenate and hydroxyl groups are coordinated with Zn and Cu. We can thus consider conichalcite and austinite as minerals with coordination bonds and we propose the formulae $Ca(CuOH)(AsO_4)$ for conichalcite and $Ca(ZnOH)(AsO_4)$ for austinite.

OLIVENITE AND ADAMITE

These minerals were included because they are typical arsenates of the isolated (AsO_4) group type and contain hydroxyl.

The adamite sample is from the Ojuela deposits, Mapimi, Mexico. The mineralogical, optical and chemical properties of adamite have been studied in detail by Mrose (1948). The sample of olivenite is from Tsumeb, Africa, and was obtained from the Mineralogical Museum of the Academy of Sciences of the USSR. This mineral has also been thoroughly described (Richmond 1940; Berry 1951).

Adamite, $Zn_2(AsO_4)OH$, and olivenite, $Cu_2(AsO_4)OH$, are orthorhombic and isostructural. The structure of adamite has been described by Kokkoros (1937) and that of olivenite by Heritsch (1938). Both minerals have a deeply deformed tetrahedron $(AsO_4)^{3-}$ as the basis of their structure. The tetrahedra have interatomic As-O distances of 1.49-1.81Å in olivenite and 1.59-1.81Å in adamite. Half of the Cu atoms in olivenite have an octahedral coordination typical of Cu^{2+}; two oxygen atoms and two hydroxyl groups surround the Cu ion, forming a square with Cu-O interatomic distances of 2.03Å for the hydroxyl (Cu-OH), and 2.12-2.34 for the oxygen in the arsenate ($Cu\text{-}OAsO_3$). The two remaining oxygen atoms are at a larger distance from the Cu atom (2.39Å). Their coordination polyhedra have the geometry of a deformed trigonal bipyramid which has five oxygen atoms and one hydroxyl group on the apices. The Cu atom is slightly shifted from the center of this bipyramid and has a medium Cu-O distance of 2.03Å for the hydroxyl (Cu-OH). The oxygen octahedra around the Cu atom are linked by a common edge. The chains are interlinked by the Cu bipyramids and the $(AsO_4)^{3-}$ tetrahedra.

The structure of adamite is analogous to the structure of olivenite except that the Zn atoms occupy Cu positions. Interatomic distances for these two minerals are given in Table 3.

The IR-spectra of our samples showed a band $\nu_3(F_2)$ split into four components (Fig. 4). The $\nu_1(A_1)$ band is not completely resolved and has the form of a shoulder at 740-750 cm^{-1}. Two intense bands appear in the $\nu_4(F_2)$ region. It is probable that the third component of the $\nu_4(F_2)$ band is located in a lower frequency region, beyond the 400 cm^{-1} limit that we could register. From these data we conclude that the symmetry of the $(AsO_4)^{3-}$ group is lowered to C_3 or C_{2v} and this concurs with the x-ray data. The deformation of the tetrahedron may be explained by the linking of the arsenate group with an atom of Cu or Zn through coordination bonds. This supposition is confirmed by the presence, in olivenite, of a stretching vibration band of Cu-O at 545 cm^{-1}, which can be observed after deuteration. The splitting of this band in adamite, which gives two components at 515 cm^{-1} and at 535 cm^{-1} for the valency vibration band of Zn-O, indicates that its octahedra have a lower symmetry.

The presence of deformation vibration bands *Me*-OH in the 900-950 cm^{-1} region confirms the coordination of the hydroxyl group with the

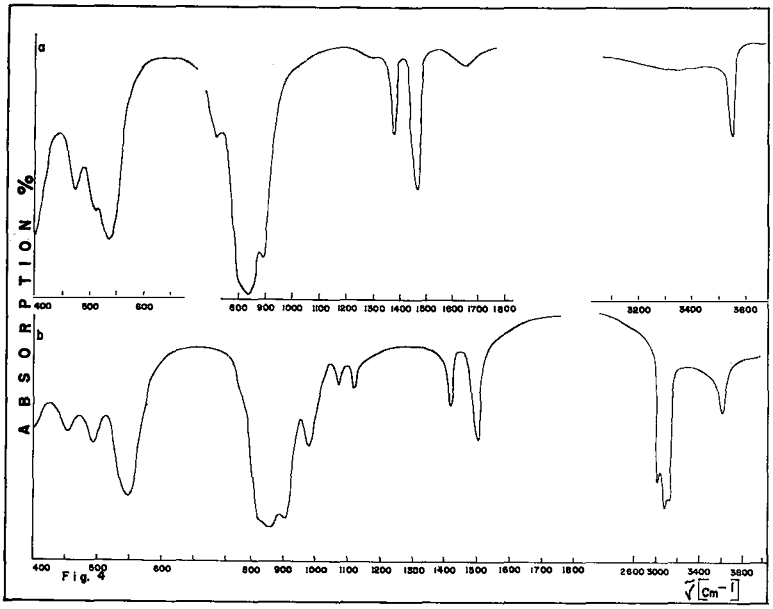

FIG. 4. Infrared spectra of (a) olivenite from Tsumeb, Africa, and (b) adamite from Ojuela, Mexico.

atom of metal. This agrees with the shift of the 950 cm^{-1} band after deuteration of conichalcite. Two sharp bands of equal intensity at 1040 cm^{-1} and at 1090^{-1} may be due to the $\nu_3(F_2)$ vibrations of the phosphate anion. Chemical analysis of the Tsumeb olivenite gave 1.5% phosphorous.

The absence of absorption bands in the 1500-1700 cm^{-1} region shows that neither olivenite nor adamite contains water. The 3440 cm^{-1} band in olivenite corresponds to the stretching vibrations of the hydroxyl groups. The high value of the band at 3580 cm^{-1} in the spectra of adamite shows that its hydroxyl groups show less indication of hydrogen bonding than those in olivenite and therefore interatomic distances between oxygen atoms O-----H-O should be larger (Table 3). X-ray data corroborate this.

From the combination of x-ray and infrared data, it is concluded that the arsenate and hydroxyl groups are coordinated with the Zn or Cu atoms. The hydroxyl groups form H-bonds with a varying degree of strength and when coordination occurs, they bind through H-bonds. It is considered that the formulae of adamite and olivenite should be represented as Cu(CuOH)(AsO_4) and Zn(ZnOH) (AsO_4) respectively.

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