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Infrared and Raman Spectra of $Na_2Cu(SO_4)_2 \cdot 2H_2O$ and $(CH_3NH_3)_2M(II)(SO_4)_2 \cdot 6H_2O$ with $M(II) = Cu$, Zn, and Ni

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FTIR and Raman spectra of $Na_2Cu(SO_4)_2 \cdot 2H_2O$ and $(CH_3NH_3)_2M(II)(SO_4)_2 \cdot 6H_2O$ with $M(II) = Cu$, Zn, and Ni are recorded and analyzed. Bands are assigned on the basis of SO_4^{2-}, $CH_3NH_3^+$, and H_2O vibrations. The lifting of degeneracies of ν_2, ν_3, and ν_4 modes and the appearance of ν_1 and ν_2 modes in the IR spectra confirm the lowering of symmetry of the SO_4^{2-} ion from T_d to C_1 in all of the title compounds. Bands obtained indicate that the distortion of the SO_4^{2-} ion in the four crystals are in the order, $(CH_3NH_3)Cu(SO_4)_2 \cdot 6H_2O > (CH_3NH_3)_2Ni(SO_4)_2 \cdot 6H_2O > (CH_3NH_3)_2Zn(SO_4)_2 \cdot 6H_2O > Na_2Cu(SO_4)_2 \cdot 2H_2O$. The appearance of NH_3 stretching modes at wavenumbers lower than the values obtained for the free ion indicates the presence of hydrogen bonds between NH_3 and SO_4^{2-} groups. The appearance of multiple bands in the bending and rocking mode regions and the broad nature of stretching modes show the existence of at least two symmetrically inequivalent water molecules in $Na_2Cu(SO_4)_2 \cdot 2H_2O$. The shifting of stretching modes to lower wavenumbers and bending modes to higher wavenumbers of water molecules confirms the existence of strong hydrogen bonds in the crystal which is in agreement with the X-ray data. Bands indicate the presence of strong hydrogen bonds involving water molecules in $(CH_3NH_3)_2Cu(SO_4)_2 \cdot 6H_2O$ and $(CH_3NH_3)_2Zn(SO_4)_2 \cdot 6H_2O$ and of lesser strength in $(CH_3NH_3)_2Ni(SO_4)_2 \cdot 6H_2O$.

INTRODUCTION

Double sulfates of divalent metals with various monovalent cations have been the subject of many investigations (1–7). Tutton's salt with empirical formula $M_2[M^{II}(H_2O)_6](SO_4)_2$, where $M^I = Rb$, Cs, K, Tl, or NH_4 and $M^{II} = Fe$, Mn, Co, Ni, Cu, Zn, Mg, V, or Ru are well known (1, 2). They crystallize in the monoclinic system with space group $P2_1/a$ with $Z = 2$, in which six water molecules are coordinated to M^{II}. Recently, great interest has been shown in the double sulfates with nonmetallic cations. Jordanovska *et al.* (3) have synthesized and characterized four double sulfates of monomethylammonium cations with divalent metals $M(II) = Co$, Ni, Zn, and Cu with chemical formula $(CH_3NH_3)_2M(II)(SO_4)_2 \cdot 6H_2O$. Interestingly, the crystal structure of these compounds differ greatly from the compounds of Tutton's family. They crystallize in the triclinic system with space group $P1$ and $Z = 1$ (3). The coordination of water molecules surrounding $M(II)$ atoms are also different from that in Tutton's salt.

An analysis of the vibrational spectra of these compounds $[(CH_3NH_3)_2M(II)(SO_4)_2 \cdot 6H_2O$ with $M(II) = Ni$, Zn, and Cu] is carried out in comparison with the spectra of another double sulfate with divalent metal cations, $Na_2Cu(SO_4)_2 \cdot 2H_2O$ to yield valuable information regarding their internal structure, intermolecular interaction, and hydrogen bonding, as the bond distances in the three crystals are not known. Crystal structure of $Na_2Cu(SO_4)_2 \cdot 6H_2O$ is well known as it has been studied by several investigators (8–14), and the Cu octahedron is distorted as in $(CH_3NH_3)_2Cu(SO_4)_2 \cdot 6H_2O$.

EXPERIMENTAL

$Na_2Cu(SO_4)_2 \cdot 2H_2O$ (here after referred to as NaCu) was prepared by dissolving equimolar quantities of

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$CuSO_4 \cdot 5H_2O$ and Na_2SO_4 in distilled water. The solution was gently warmed and concentrated at 313 K (14). After 24 h, well-formed crystals of NaCu were obtained. Partially deuterated analogue of NaCu (80%) was prepared by dissolving a small quantity of NaCu in excess of 99.99% pure heavy water. The solution was evaporated under a vacuum desiccator. The process was repeated to enhance the percentage of deuteration.

$(CH_3NH_3)_2M(II)(SO_4)_2 . 6H_2O$ with M(II) = Zn, Ni, and Cu (abbreviated as CNZn, CNNi, and CNCu, respectively) were prepared by evaporating the aqueous solution containing the corresponding metal sulfate and monomethylammonium sulphates in the ratio 1 : 3 at ambient temperature (300 ± 3K) (3).

Raman spectra of polycrystalline samples of NaCu, CNZn, CNNi, and CNCu taken in capillary tubes were recorded using a 1401 Spex Raman spectrometer equipped with a Spectra Physics 165.08 argon-ion laser. Spectra were recorded using both 514.5- and 488.0-nm lines at a resolution better than 3 cm^{-1}. The number of bands obtained for CNNi is less than in other compounds and also with reduced intensity. This may be due to the fact that CNNi is green in color and slightly fluorescing. Raman spectra are redrawn conforming to the original spectra (intensities rescaled relative to the original spectra) obtained for the crystals and are shown in Figs. 1–3. The FTIR spectra (Figs. 4 and 5) of these compounds and partially deuterated analogue of NaCu (abbreviated at NaCuD) were recorded using a Bruker IFS-66V–FTIR spectrometer. In the far-IR region (50–400 cm^{-1} region) polyethylene pellets were used and in the mid-IR region (400–4000 cm^{-1} region) KBr pellets were used.

FACTOR GROUP ANALYSIS

$Na_2Cu(SO_4)_2 \cdot 2H_2O$ crystallizes in the monoclinic system with space group $P2_1/c$ and $Z = 2$ (14). The Cu octahedron has two Cu–O_w = 1.95 Å and two Cu–O (SO_4) = 1.99 Å. The remaining two Cu–O (SO_4) distances have a longer value 2.41 Å, making CuO_6 a distorted octahedron. The Cu octahedron and the sulfate tetrahedron are bonded by common oxygen atoms and can be regarded as $[Cu(SO_4)_2 \cdot 2H_2O]$ chains along the c axis. The Na atoms occupy the free positions between the chains. Each of the Na atoms forms a sevenfold coordination with six oxygen atoms and one water molecule. Hydrogen bridges between the H_2O molecule and two sulfate groups, form $[H_2O(SO_4)]^{2-}$ chains. In NaCu, SO_4^{2-} anions, Na atoms, and H_2O molecules occupy C_1 sites and Cu atoms occupy C_i sites. Factor group analysis of the compound has been carried out by the correlation method developed by Fateley *et al.* (15). Excluding acoustic modes at $k = 0$, 111 optical modes under C_{2h} factor group are distributed as under,

$$\Gamma_{NaCu} = 27A_g + 27B_g + 29A_u + 28B_u$$

Among the methylammonium compounds CNNi and CNZn are isostructural, whereas CNCu has a different

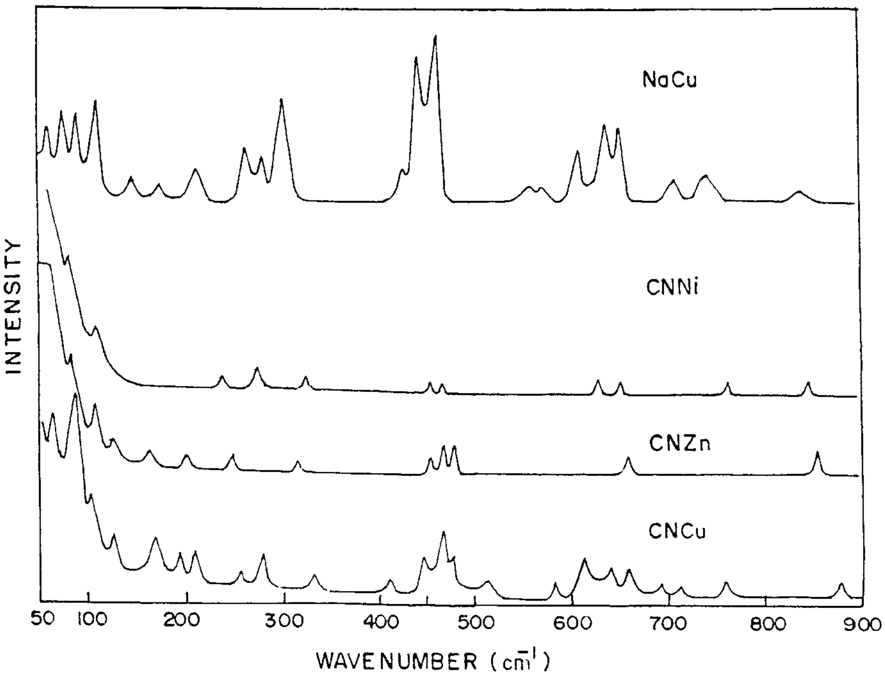


FIG. 1. Raman spectra of (a) CNCu, (b) CNZn, (c) CNNi, and (d) NaCu in the 50–900 cm^{-1} region.

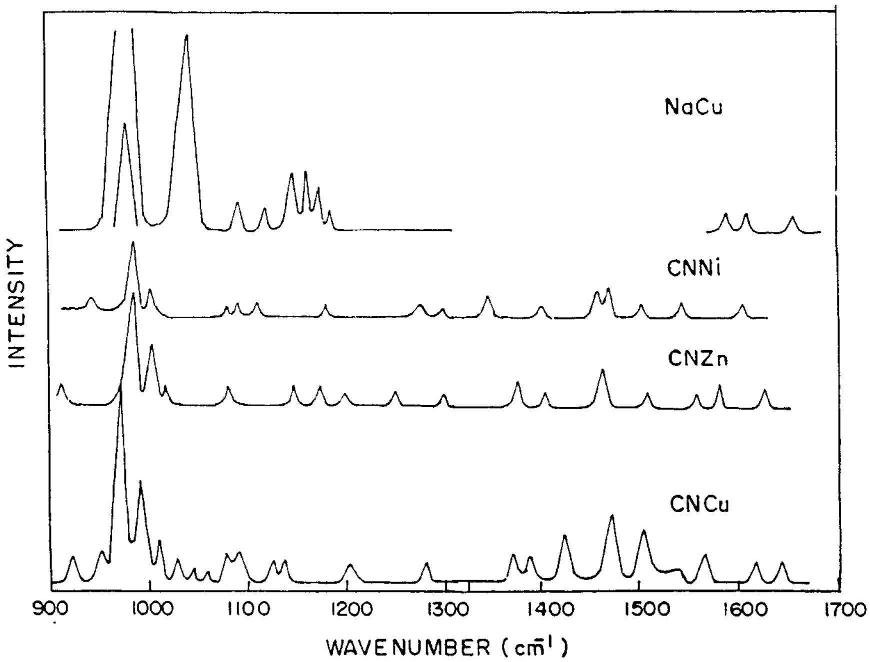


FIG. 2. Raman spectra of (a) CNCu, (b) CNZn, (c) CNNi, and (d) NaCu in the 900–1700 cm^{-1} region.

structure. In CNNi and CNZn, the divalent metal cations are surrounded by four water molecules and two O atoms from the two SO_4 groups in the form of an almost regular octahedron. In CNCu, an elongated octahedron is formed around the Cu^{2+} cation by four water molecules and two oxygen atoms from the two sulfate groups. Cu–O distances are longer than Cu–O_w distances. Factor group analysis predicts 132 fundamentals for each compound at $k = 0$, excluding the acoustic modes. They are distributed as,

$$\Gamma_{CN(Ni,\,Zn,\,and\,Cu)} = 66A_g + 66A_u.$$

RESULTS AND DISCUSSION

Correlation diagrams for different ions in Tables 1 and 2 map out the site splitting and factor-group splitting in the crystals. Assignment of bands (Table 3) is carried out in terms of SO_4^{2-}, $CH_3NH_3^+$, and water vibrations.

SO_4^{2-} Vibrations

The normal modes of vibration of a free tetrahedral SO_4^{2-} ion under T_d symmetry have frequencies at 981, 451, 1104,

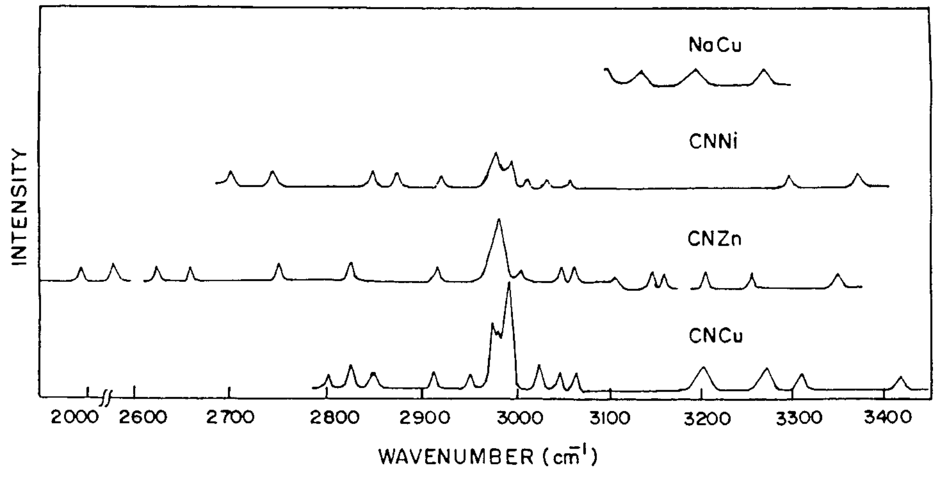


FIG. 3. Raman spectra of (a) CNCu, (b) CNZn, (c) CNNi, and (d) NaCu in the 2000–3500 cm^{-1} region.

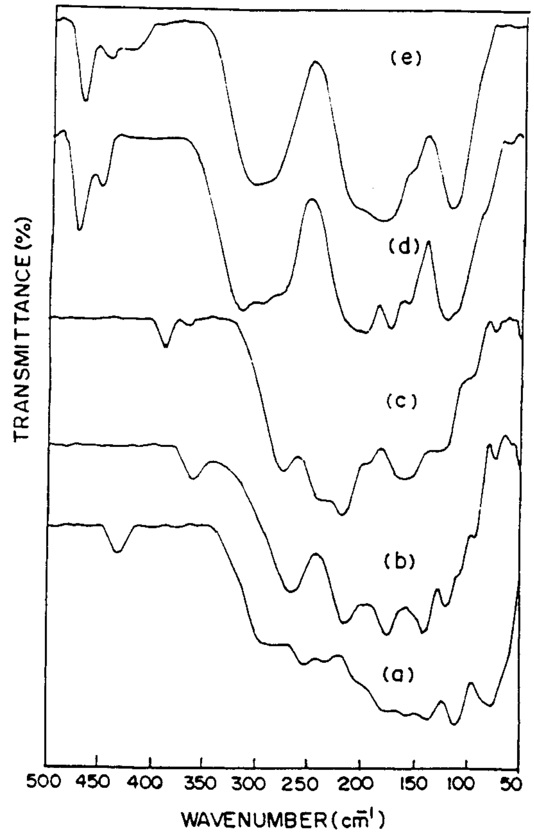


FIG. 4. FTIR spectra of (a) CNCu, (b) CNZn, (c) CNNi, (d) NaCu, and (e) NaCuD in the 50–500 cm^{-1} region.

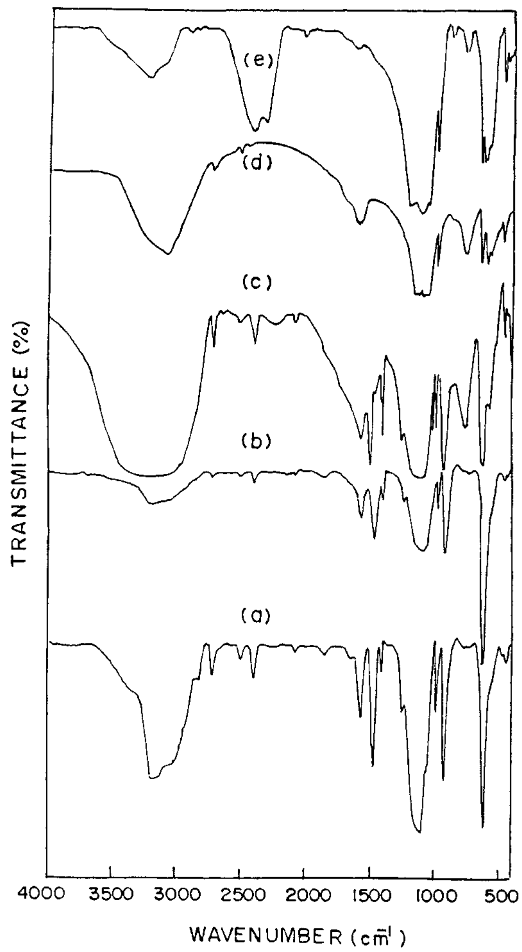


FIG. 5. FTIR spectra of (a) CNCu, (b) CNZn, (c) CNNi, (d) NaCu, and (e) NaCuD in the 400–4000 cm^{-1} region.

and 613 cm^{-1} for $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$, and $\nu_4(F_2)$ modes, respectively. All of these modes are Raman active, whereas ν_1 and ν_2 modes are IR inactive (16).

$Na_2Cu(SO_4)_2 \cdot 2H_2O$

The nondegenerate symmetric stretching mode (ν_1) of SO_4^{2-} appears as a very intense band at 989 cm^{-1} in the Raman spectrum and as an intense band at 992 cm^{-1} in the FTIR spectrum. The triply degenerate asymmetric stretching mode (ν_3) of the SO_4^{2-} ion appears with large splitting in both FTIR and Raman spectra (Table 3).

Usually the ν_3 mode of SO_4^{2-} appears with weak or medium intensity in the Raman spectrum and with very high intensity in the infrared spectrum. The Raman band at 1045 cm^{-1} exhibits very high intensity in this crystal. In $(NH_4)_3H(SO_4)_2$ (17, 18), the ν_1 mode of SO_4^{2-} is observed around 1080 cm^{-1}. Therefore, it may appear that there is an ambiguity whether this mode belongs to ν_3 or ν_1. The ν_1 mode is usually inactive and the ν_3 mode active in the IR spectrum. In the case of the 1045-cm^{-1} band in Raman spectrum, a very intense band is observed at 1052 cm^{-1} in the IR spectrum indicating that it is a ν_3 mode. In the $Na_2Cu(SO_4)_2 \cdot 2H_2O$ crystal, hydrogen bridges exist between two SO_4 groups and water molecules forming $(H_2OSO_4)^{2-}$ chains. Hence, there is a possibility for the presence of an HSO_4^- ion in the crystal. The symmetric stretching vibration of the HSO_4^- ion appears at 1051 cm^{-1} with high intensity in the Raman spectra of the aqueous solution (19, 20). The HSO_4^- ion has a C_{3v} symmetry and the ν_1 mode can be IR active in such a system. On deuteration, wavenumber value and intensity of this mode will show considerable change. But the band at 1052 cm^{-1} in the FTIR spectra of the partially deuterated (80%) analogue of NaCu remains unaffected. Also, one can expect S–OH stretching bands with appreciable intensity in the 800–900 cm^{-1} region of the Raman spectrum for the HSO_4^- ions (20, 21). In the present study only a very weak band is observed at about 840 cm^{-1} in the Raman spectrum. In the FTIR spectrum, a medium intense band is observed at about 875 cm^{-1} in this region. On deuteration the intensity of this band is considerably reduced. In the HSO_4^- ion these modes are not observed in the IR spectrum (21). Therefore,

TABLE 1

Correlation of the Internal Vibrational Modes of SO_4^{2-} and H_2O in $Na_2Cu(SO_4)_2 \cdot 2H_2O$

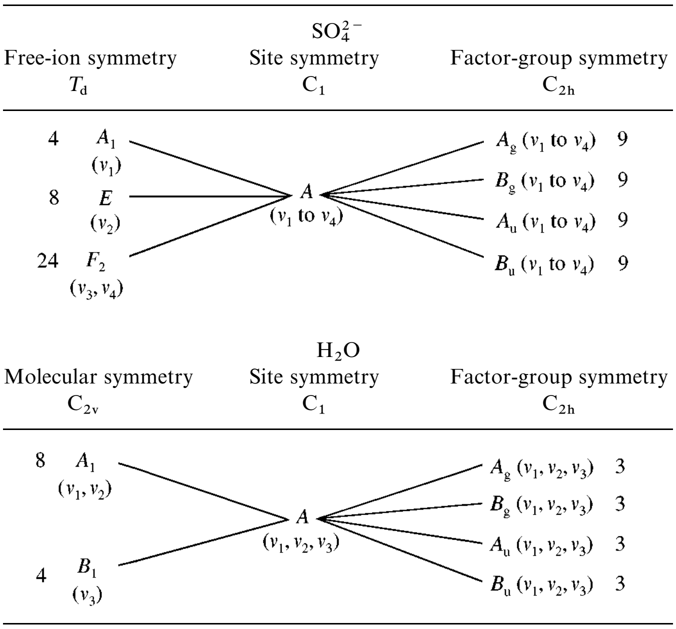
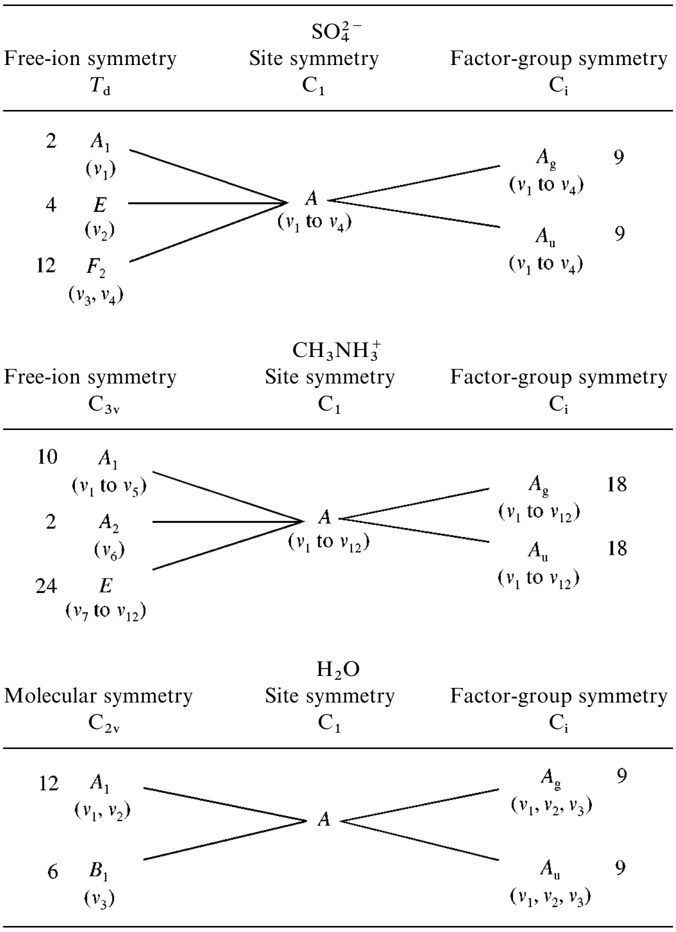


TABLE 2

Correlation for the Internal Vibrational Modes of SO_4^{2-}, $CH_3NH_3^+$, and H_2O in $(CH_3NH_3)_2M(II)(SO_4)_2 \cdot 6H_2O$ (M(II)= Cu, Zn, Ni)



they are assigned to the librational modes of water. Hence, it can be concluded that the bands at 1045 cm^{-1} do not belong to the ν_1 mode of the SO_4^{2-} or HSO_4^- ion.

The doubly degenerate bending mode (ν_2) of SO_4^{2-}, exhibits additional splitting apart from the lifting of degeneracy in both FTIR and Raman spectra. The degeneracy of the triply degenerate bending (ν_4) mode is lifted in the Raman spectrum while it is partially retained in the FTIR spectrum.

CNZn, CNNi, and CNCu

The ν_1 mode of SO_4^{2-} is observed in CNZn as an intense band at 985 cm^{-1} and a medium-intensity band at 1004 cm^{-1} in the Raman spectrum and as a weak band at 982 cm^{-1} in the FTIR spectrum. In CNNi, the intensity of bands around 985 and 1001 cm^{-1} is reduced in the Raman spectrum. This mode is also split in the FTIR spectrum and two medium intense bands around 984 and 1002 cm^{-1} are observed. In the Raman spectrum of CNCu, the ν_1 mode exhibits large splitting and three bands around 973, 993, and 1006 cm^{-1} are obtained. But, only a medium intense band is observed in the FTIR spectrum in this region.

The asymmetric stretching mode ν_3 of the SO_4^{2-} ion shows large splitting in the Raman spectra of all of the compounds. In the FTIR spectra, a very intense broad band is observed in CNCu at 1112 cm^{-1} and in CNNi at 1103 cm^{-1}. In the zinc compound, the intensity of this band is less and it is observed around 1100 cm^{-1}.

The doubly degenerate bending mode ν_2 of SO_4^{2-} appears with considerable splitting in both spectra for all three compounds. In the FTIR spectra of CNCu and CNZn, the asymmetric bending mode (ν_4) appears as a very intense broad band around 618 cm^{-1} while in CNNi, the degeneracy of this mode is partially lifted and it appears as a very intense band at 617 cm^{-1} and an intense band at 576 cm^{-1}.

In all of the title compounds the sulfate ions occupy the general sites C_1 whose symmetry is much lower than the free ion symmetry T_d of SO_4^{2-} ion. Therefore, SO_4^{2-} ion may be distorted in the crystal. This accounts for the lifting of degeneracies of the ν_2, ν_3, and ν_4 modes and the appearance of ν_1 and ν_2 modes in the IR spectrum in all of the crystals. In NaCu, there are four SO_4 units in the Bravais cell while there are only two SO_4 units each in the other three crystals. But the splitting for ν_2, ν_3, and ν_4 modes are identical in all four crystals except in CNZn where the ν_4 mode gives only one band and the ν_3 mode gives fewer components. This shows that more splitting of modes apart from the lifting of degeneracies is obtained in CNCu and CNNi crystals, with two SO_4 units. Moreover, the nondegenerate symmetric stretching mode ν_1 appears as two factor-group multiplets in the Raman spectra of CNNi and CNZn while in CNCu, ν_1 appears as three multiplets. In NaCu only one band is obtained for this mode. There are six water molecules and two NH_3 groups in CNNi, CNZn, and CNCu crystals and they can form hydrogen bonds with oxygen atoms in the SO_4 groups. This causes the distortion of the SO_4 tetrahedra to be large in these three monomethylammonium compounds causing the splitting of all the modes. In CNNi and

TABLE 3
Spectral Data (cm^{-1}) and Band Assignments

$Na_2Cu(SO_4)_2 \cdot 2D_2O$	$Na_2Cu(SO_4)_2 \cdot 2H_2O$		$(CH_3NH_3)_2Cu(SO_4)_2 \cdot 6H_2O$		$(CH_3NH_3)_2Zn(SO_2)_2 \cdot 6H_2O$		$(CH_3NH_3)_2Ni(SO_4)_2 \cdot 6H_2O$		Assignments
FTIR	FTIR	Raman	FTIR	Raman	FTIR	Raman	FTIR	Raman	
1	2	3	4	5	6	7	8	9	10
50vw		55m			51m		51m		
61vw	63w	70m		62m	59w		58w		
77vw	86sh	80m	77vs	85s	73w	85vw	74w	83vw	
	110sh	100s	110vs	100w	94s	105w	92m	107vw	
120vs	122vs		137vs	125w	121vs	120vw	129s		
		145w	156s		142vs				
	160vs			169m		165vw	160vs		
188vs	176vs	175w	175s		176vs				External modes
	199vs			196vw		200vw	194sh		
	210sh	210w		212w	216vs		217vs		
			233s			245vw	240sh	240vw	
		260m	253s	258vw	265vs				
	275sh	280w		278w			275vs	273w	
306vs	296vs	300s							
	315vs			330vw		320vw	347vw	324w	
370vw	393vw		380vw		361m		365w		
							387m		
401vw	414vw		400vw	409vw			410m		
425sh	428vw	430sh	431m	440m	450vw	455vw		455vw	
445m	450m	444s	450w	469m	464vw	465w	461m	465vw	ν_2SO_4
471s	473s	464s	478w	475w		474w			
570sh	570s	560wbr		510w	536vw			500vw	
		585w							Wagging of H_2O
607vs	603vs	615m	618vs	580w	618vs		576s		
620vs				610w			617s	630vw	ν_4SO_4
643vs	646vs	645m		640w				655vw	
		655m		659w		660vw			
				697vw					
		715vw		717vw					
770w	776vs	740wbr	777w	764w	742w		761s	765vw	Rocking H_2O
882w	875m	840vw							
				883m		851vw		848vw	ν_S C–N (ν_5)
			926vs	920w	922m	915w	922vs	943vw	
				952m					NH_3 rocking (ν_{12})
992s	992s	989vvs	984m	973vs	982w	985s	983m	985m	
				993s		1004m	1002m	1001w	ν_1SO_4
				1006m					
				1029w		1015vw			ν_{as} C–N
				1040w					
1053vs	1052vs	1045vs		1057w				1060vw	
	1084vs	1090w		1083m		1082vw			
1109vs	1111vs	1128w	1112vsbr	1093m	1100mbr		1103vsbr	1117vw	ν_3SO_4
	1148vs	1150m		1122w		1145w			
1197vs		1162m		1136w		1175w		1185vw	
		1175w							
		1182w							
				1200w		1200vw			
			1256m	1280vw	1254w	1250vw	1255s	1280vw	CH_3 rocking (ν_{11})
						1300vw		1300vw	
				1371w		1380w		1350w	
				1380w	1408w	1410w	1409s	1410w	$\delta_S CH_3$ (ν_4)

Table 3—*Continued*

$Na_2Cu(SO_4)_2 \cdot 2D_2O$	$Na_2Cu(SO_4)_2 \cdot 2H_2O$		$(CH_3NH_3)_2Cu(SO_4)_2 \cdot 6H_2O$		$(CH_3NH_3)_2Zn(SO_2)_2 \cdot 6H_2O$		$(CH_3NH_3)_2Ni(SO_4)_2 \cdot 6H_2O$		Assignments
FTIR	FTIR	Raman	FTIR	Raman	FTIR	Raman	FTIR	Raman	
1	2	3	4	5	6	7	8	9	10
			1417w	1420m	1423w				
			1477vs	1470m	1487m	1465w	1460w	1465w	$\delta_{as}CH_3$ (ν_{10})
			1490sh				1501vs	1475vw	
				1506m		1507w		1507vw	
				1553vw				1548vw	
			1575s	1564w	1580m	1560vw	1576vs		NH_3 deformation
				1584vw		1580w			(ν_3, ν_9) and
1631w	1614s	1590w		1618w		1630w		1616w	
	1700sh	1610w	1650sh	1641w	1683sh				ν_2 H_2O
		1660w	1641w			1720vw			
			1855w		1856w	1990vw			
2032vw			2078w		2083w	2030vw	2071w		
	2363w		2263vw		2150vw		2230wbr		
			2407m		2400w		2395m		Combinations
			2506w		2514w	2622w	2512w	2700vw	and overtones
2851vw			2725m		2725w	2660w	2716m	2740vw	
2922vw						2748vw			
2323vs									ν_1 and ν_3 D_2O
2415vs									
				2800w					
				2823w		2824w			
			2832m	2849vw				2848vw	
				2915w	2875w			2870w	ν_S CH_3 (ν_2)
			2950sh	2944w		2917w		2920vw	
				2975sh				2975wbr	ν_S NH_3 (ν_1)
			3015sh	2990vs		2980s		2995w	
				3026w		3010vw	Very intense	3010vw	ν_{as} CH_3 (ν_8)
				3046w		3045w	broad band	3035vw	and
				3100w		3060w	extending	3060vw	ν_{as} NH_3 (ν_7)
			3190vsbr		3194mbr		from 2850 to		
	3092vs	3100w		3203m		3210vw	3650 cm^{-1}		
		3140w		3272w		3260vw		3300vw	ν_1 and ν_3 H_2O
3221m		3200w	3330m	3313w		3350vw		3380w	
		3280w		3423w					

Note. v, very; s, strong; m, medium; w, weak; br, broad; sh, shoulder.

CNZn the metal oxygen coordination (consisting of four O atoms of water molecules and two O atoms of SO_4 groups) leads to the formation of a regular octahedron (3) around the metal atom. In CNCu the two oxygen atom of sulfate groups are at longer distances causing a distorted octahedron. This in turn leads to more distortion of SO_4^{2-} ions and consequently the ν_1 mode splits into more components in the CNCu crystal. The distortion of SO_4^{2-} ion in all four crystals is in the order CNCu > CNNi > CNZn > NaCu. Even though a distorted CuO_6 octahedron is present in the NaCu crystal, only two water molecules are available for forming hydrogen bonds with the oxygen atom of SO_4 groups and, hence, the distortion of SO_4^{2-} ion is lowest in that crystal.

$CH_3NH_3^+$ Vibrations

A free $CH_3NH_3^+$ ion has a C_{3v} symmetry and has 18 normal modes, which are distributed as

$$\Gamma_{int} = 5A_1 + A_2 + 6E.$$

These bands are distributed as ν_1 to ν_{12} and the assignments are made in comparison with the assignments given for this ion in $CH_3NH_3NO_3$, $CH_3NH_3ClO_4$, $(CH_3NH_3)_2ZnBr_4$, and $(CH_3NH_3)_2ZnCl_4$ (22–25).

The symmetric N–H stretching mode (ν_1) is observed in the Raman spectra as a very intense band around 2990 cm^{-1} with a shoulder at 2975 cm^{-1} in CNCu, while their intensity is considerably reduced in CNNi. In CNZn only an intense band at 2980 cm^{-1} is obtained in the Raman spectrum. The symmetric C–H stretching mode is observed as a few weak bands in the 2820–2950 cm^{-1} region in the Raman spectra for all three compounds. The Raman bands in the 3000 to 3100 cm^{-1} are assigned to the asymmetric stretching modes of CH_3 and NH_3. In the FTIR spectra, these modes are not resolved. In CNCu a very intense broad band is observed at 3190 cm^{-1} with a shoulder at 3015 cm^{-1}. In CNZn a medium intense broad band is observed around 3192 cm^{-1} extending from 2850 to 3300 cm^{-1}. A very intense, broad band extending from 2850 to 3650 cm^{-1} is observed in CNNi. The intensity of this mode is larger than that observed for the other two compounds. A number of bands observed in the 1800 to 2750 cm^{-1} region are assigned to combinations and overtones.

In compounds containing NH_3 groups adjacent to CH_3 groups, the C–H stretching frequencies shift to lower values (26). This is observed in these crystals as C–H symmetric stretching modes appear at lower wavenumbers up to 2823 cm^{-1}. NH_3 stretching modes are also observed at wavenumbers lower than the values obtained for the free ion (3336 and 3417 cm^{-1}) (16). This indicates that hydrogen atoms of NH_3 form hydrogen bonds with the oxygen atom of the SO_4 groups.

Water Vibrations

A very intense broad band extending from 3475 to 2934 cm^{-1} is obtained in the FTIR spectrum for NaCu. On deuteration, the intensity of this band is reduced and new bands appear at 2415 and 2323 cm^{-1}. In the Raman spectrum, two weak bands are observed in this region. In the H_2O bending mode region of NaCu an intense band is observed around 1614 cm^{-1} with a shoulder around 1700 cm^{-1} in the FTIR spectrum. In the Raman spectrum, three weak bands are obtained in this region. The appearance of multiple bands in the H_2O bending mode region and the broad nature of stretching modes indicate the existence of, at least, two symmetrically inequivalent water molecules in NaCu. The appearance of stretching modes at wavenumbers lower than those of a free water molecule and the bending modes at higher wavenumbers confirm the existence of strong hydrogen bonds in the crystal in agreement with the X-ray data (14).

In CNCu, CNZn, and CNNi, water stretching modes and the stretching modes of CH_3 and NH_3 appear as a broad and intense band. In the bending mode region of water, NH_3 bending modes also appear. Strong NH_3 bands mask the H_2O bending modes. The fact that the stretching modes are observed below 3300 cm^{-1} in both CNCu and CNZn indicates that strong hydrogen bonds exist in both crystals. The bands in CNNi start near 3500 cm^{-1} indicating weaker hydrogen bonds in the crystal. In Tutton salts, three crystallographically distinct water molecules are identified from the Raman and IR spectra (6, 7, 27, 28). In the monomethylammonium crystals this cannot be identified, as the bands are not well resolved.

Librational modes viz., rocking, twisting, and wagging modes of water molecules can be expected in the 500–900 cm^{-1} region (29). In the FTIR spectra of NaCu an intense band at 776 cm^{-1} and a medium-intensity band at 875 cm^{-1} are obtained for the rocking mode of water molecules (30). Upon deuteration, these bands lose most of the intensity and a new band appears around 620 cm^{-1}. The appearance of two bands for the rocking modes also supports the presence of two symmetrically inequivalent water molecules in the NaCu crystal. In the CNCu and CNZn the corresponding bands are observed with weak intensity around 777 and 742 cm^{-1}, respectively, while an intense band is obtained in CNNi at 761 cm^{-1}.

In NaCu crystal an intense band is observed around 570 cm^{-1} in the FTIR spectrum. The intensity of this band decreases considerably when the compound is deuterated. Therefore, this band is assigned to the H_2O wagging mode.

CONCLUSIONS

The lifting of degeneracies of ν_2, ν_3, and ν_4 modes and the appearance of ν_1 and ν_2 modes in the IR spectra confirm the lowering of symmetry of SO_4^{2-} ion from T_d to C_1 in all of the title compounds. Bands obtained indicate that the distortion of SO_4^{2-} ion in the four crystals are in the order

$$(CH_3NH_3)_2Cu(SO_4)_2\cdot 6H_2O > (CH_3NH_3)_2Ni(SO_4)_2\cdot 6H_2O$$
$$> (CH_3NH_3)_2Zn(SO_4)_2\cdot 6H_2O > Na_2Cu(SO_4)_2\cdot 2H_2O$$

The appearance of NH_3 stretching modes at wavenumbers lower than the values obtained for the free ion indicates the presence of hydrogen bonds between NH_3 and SO_4 groups.

The appearance of multiple bands in the bending and rocking mode regions and the broad nature of stretching modes show the existence of at least two symmetrically inequivalent water molecules in $Na_2Cu(SO_4)_2\cdot 2H_2O$. The shifting of stretching modes to lower wavenumbers and bending modes to higher wavenumbers of water molecules confirm the existence of strong hydrogen bonds in the crystal which is in agreement with the X-ray data. Bands indicate the presence of strong hydrogen bonds involving water molecules in $(CH_3NH_3)Cu(SO_4)_2\cdot 6H_2O$ and $(CH_3NH_3)_2Zn(SO_4)_2\cdot 6H_2O$ and of lesser strength in $(CH_3NH_3)_2Ni(SO_4)_2\cdot 6H_2O$.

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