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Infrared Spectra of the Addition Compounds of Trimethylamine Oxide with Zinc, Cadmium and Mercuric Halides in the Range 1500—250 cm^{-1}

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Infrared spectra were taken in the region 4000—250 cm^{-1} for trimethylamine oxide complexes of the type ZnX_2L_2 and Cd(or Hg)X_2L($L=(CH_3)_3NO$ and X=Cl, Br or I). Two new bands at about 550 and 400 cm^{-1} were observed for all complexes. The zinc complexes gave rise to more bands at about 955 and 270 cm^{-1}. Except for these bands, no appreciable change was observed in the vibrational frequencies of trimethylamine oxide upon coordination. These results suggest that the complexes form a tetrahedral arrangement about a metal atom with weak coordinate bonds, and that the crystals of the zinc complexes consist of monomers and those of the cadmium and the mercury complexes of halogen bridged dimeric molecules $[MX_2L]_2$.

In previous infrared and Raman studies[1)] of trimethylamine oxide dihydrate, assignments of vibrational frequencies were based upon the polarization properties of the Raman lines and normal coordinate treatment. According to the results, the N–O bond of trimethylamine oxide in the solid state absorbs at 936 cm^{-1}. This value is in the same frequency region as for the N–O bonds of unconjugated oximes. The N–O stretching force constant obtained for trimethylamine oxide, 3.580 mdyn/Å,

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was also very close to values ranging from 3.8 to 4.0 mdyn/Å for unconjugated oximes.[2,3] From these results, the N–O bond of trimethylamine oxide was concluded to have a pure single bond character in accordance with conclusions drawn from the results of X-Ray structure analysis[4] and electric dipole moment measurement.[5]

Recently, metal complexes with tertiary phosphine oxides[6] and tertiary arsine oxides[7] were prepared and studied by means of electronic spectra, infrared spectra, magnetic measurements and so on. It is known that the oxygen atom of tertiary amine oxide behaves as an electron donor and forms a coordinates to metal atoms.[8-11] Since the possibility of π-bond character is not present in trimethyl amine oxide, these studies were undertaken to compare the coordination of oxygen atoms in trimethyl amine oxide complexes and other types of complexes. However, the bond characters and molecular configurations in these kinds of complexes are not systematically interpreted yet.

In the present infrared study, addition compounds between trimethylamine oxide and the halides of the 2nd *b*-subgroup elements were dealt with, and attention was focused on the effect of coordination on ligand vibrations.

Experimental

Preparation. $ZnBr_2$ *and* ZnI_2 *Addition Compounds.* A solution of 0.01—0.02 mol of $(CH_3)_3NO \cdot 2H_2O$ in about 50 m*l* of ethanol was slowly added to a solution of 0.01 mol zinc halide in about 50 m*l* of ethanol. Needle crystals were formed in from a few hours to a few days. These crystals were collected, washed several times with ethanol and dried over phophorus pentoxide for several days. These complexes are slightly soluble in water, methanol and ethanol at room temperature, but decompose in warm solutions. Found: Zn, 17.4; C, 19.2; H, 4.85; N, 7.07%. Calcd for $ZnBr_2[(CH_3)_3NO]_2$: Zn, 17.41; C, 19.20; H, 4.83; N, 7.46%. Found: Zn, 14.0; C, 15.24; H, 3.91; N, 5.88%. Calcd for $ZnI_2[(CH_3)_3NO]_2$: Zn, 13.93; C, 15.34; H, 3.87; N, 5.97%.

$CdCl_2$, $CdBr_2$ *and* CdI_2 *Addition Compounds.* These compounds were prepared by the same procedure as that used for the zinc complexes. Precipitates were formed immediately from solutions. All complexes are soluble in water, methanol and ethanol. Found: Cd, 42.6; C, 14.22; H, 3.60; N, 5.21%. Calcd for $CdCl_2[(CH_3)_3NO]$: Cd, 43.5; C, 13.94; H, 3.51; N, 5.24%. Found: Cd 33.0%. Calcd for $CdBr_2[(CH_3)_3NO]$: Cd, 32.4%. Found: Cd, 25.1%. Calcd for $CdI_2[(CH_3)_3NO]$: Cd, 25.5%.

$HgCl_2$ *and* $HgBr_2$ *Addition Compounds.* The procedure of preparation was the same as for the zinc and cadmium complexes. White needle crystals were formed in a few minutes after the solutions were mixed. They decompose in water solutions. Found: Hg, 57.1%. Calcd for $HgCl_2[(CH_3)_3NO]$: Hg, 57.9%. Found: Hg, 46.7%. Calcd. for $HgBr_2[(CH_3)_3NO]$: Hg, 46.1%.

Measurement. Infrared spectra were taken using a grating infrared spectrophotometer model DS-402G of the Japan Spectroscopic Co., Ltd. The samples were run as Nujol mulls in the region 4000—250 cm^{-1}, and the regions of Nujol absorptions were examined with hexachlorobutadiene mulls. The 3 μ region was employed for checking the absence of hydrated water molecules in the complexes.

The observed frequencies for the complexes are listed in Table 1 together with those for trimethylamine oxide.[1]

Results and Discussion

All bands due to trimethylamine oxide remain practically unaltered in the spectrum of every complex under investigation. In addition, two new bands appear at about 550 and about 400 cm^{-1}. These additional bands are also observed at approximately the same position irrespective of the type of compounds. The zinc complexes give rise to more absorption bands at about 955 and about 270 cm^{-1}. Rodley *et al.* also dealt with this type of zinc halide complex, but mentioned nothing about these bands.[11] Bands at 946 and 492 cm^{-1} for the complex of cadmium iodide are relatively wide and are probably composite bands corresponding to the doublet bands of the other cadmium complexes.

Vibrations Associated with the Ligand. The cadmium and mercury complexes have two bands near 950 cm^{-1} corresponding to the degenerate C–N stretching vibration, $\nu(C_3N)$, and the N–O stretching vibration, ν(N–O), of the ligand, while the zinc complexes have three bands near 950 cm^{-1}. Kida *et al.*[12a] also observed two N–O stretching bands, ν(N–O), at about 1210 and about 1205 cm^{-1}, only for zinc and copper complexes of pyridine *N*-oxide, the former of which, $Zn(PyO)_2Cl_2$, is analogous to $ZnCl_2[(CH_3)_3NO]_2$ in its formula.

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TABLE 1. OBSERVED FREQUENCIES FOR THE COMPLEXES OF TRIMETHYLAMINE OXIDE WITH THE METAL HALIDES (in cm^{-1})

L*	$ZnBr_2\cdot L_2$	$ZnI_2\cdot L_2$	$CdCl_2\cdot L$	$CdBr_2\cdot L$	$CdI_2\cdot L$	$HgCl_2\cdot L$	$HgBr_2\cdot L$
1482	1482 s	1480 s	1481 s	1480 s	1476 s	1476 s	1473 s
1472	1473 s	1474 s	1470 s	1465 s	~1460 sh	1456 s	1451 s
1457	1459 s	1456 s	1462 s	1459 s	1454 s	1427 w	1434 w
1442	1435 m	1435 m	1455 s	1455 s	1393 m	1403 m	1400 s
1432	1428 m	1428 m	1425 w	1425 m			
1398	1390 s	1392 s	1413 m	1412 m			
			1397 w	1386 w			
1240	1233 s	1229 s	1244 s	1241 s	1232 s	1230 m	1226 m
1124	1116 m	1115 m	1132 w	1128 w	1121 w	1124 m	1115 m
	955 s	953 sh					
946	946 s	945 s	956 s	953 s	946 vs	942 s	942 s
936	940 s	942 sh	947 s	942 s		935 s	926 s
756	766 s	764 s	762 s	757 s	760 s	757 m	752 m
	555 s	550 s	542 s	537 s	528 m	542 s	540 s
497	489 m	487 m	500 m	495 sh	492 m	485 m	486 m
469	476 s	475 s	483 s	481 s		470 s	473 s
380	402 m	395 m	403 m	402 m	400 m	395 m	395 m
	378 m	374 m	388 m	388 m	380 m	382 m	382 m
	276 m, b	274 m					

* $L\equiv(CH_3)_3NO$

Generally, Zn(II) has a very strong tendency to appear in tetrahedral environments as indicated by the following examples: $ZnCl_2(NH_3)_2$ and $ZnBr_2(NH_3)_2$ crystals,[13] and $ZnCl_2$[thiourea]$_2$.[14] The zinc atoms of the addition compounds studied here probably follow this general tendency of coordination. If the two N-O bonds are arranged in close proximity to each other so as to have no center of symmetry, the ν(N-O) bands are possibly observed as two bands, even though the frequency separation between them might be small. Unlike Zn complexes, Cd and Hg complexes in the crystalline state form either a tetrahedral or octahedral arrangement about a metal atom according to the constitution of the complexes. The crystal of the type LCd(or Hg)X_2, such as [trimethyl-phosphine]$CdBr_2$ consists of halogen bridged dimeric molecules expressed by $L_2(CdX_2)_2$.[15] The single dimeric molecules, then, have a center of symmetry and approximately tetrahedral arrangement about the metal atoms. The type of Cd and Hg complexes treated in the present study is the same as the type compounds mentioned above. Therefore, it is quite probable that the crystals of the complexes in question are also built from dimeric molecules with a center of symmetry. Then, only one ν(N-O) should be observed. The metal-halogen stretching frequencies ν(M-X) of some complex halides of Zn, Cd and Hg were discussed by Coates and Ridley, and were successfully interprcted from this view point of structures as described above.[15]

It is reasonable to consider that the band near 400 cm^{-1} was caused by splitting of the degenerate vibration of the ligand upon coordination. Similarly, it is probable that the degenerate C-N stretching vibration of the ligand near 950 cm^{-1} splits appreciably and gives rise to the additional bands for zinc complexes. Furthermore, a band near 550 cm^{-1} is due probably to the splitting of the degenerate N-O rocking vibration of the ligand at 497 cm^{-1}.

No appreciable change in observed frequencies for trimethylamine *N*-oxide could be seen upon coordination to Zn, Cd and Hg atoms, except for some splittings of the degenerate vibrations. Similar phenomena were observed for $M[(CH_3)_3NO]_4^{2-}$ by Kida[9] and Drago *et al.*,[10] and for $Zn[(CH_3)_3NO]_2X_2$ by Rodley *et al.*[11] This is quite interesting upon comparison with changes in the vibrational frequencies of pyridine *N*-oxide or tertiary phosphine oxides upon coordination. The ν(N-O) of pyridine *N*-oxide[12] are lowered by about 45 cm^{-1} and the ν(P-O) of tertiary phosphine oxides[6b] by about 50 cm^{-1} upon coordination. These frequency shifts can be explained by a decrease in the double bond character of the N-O or P-O bonds upon coordination. Such an origin of frequency lowering can hardly be found for trimethylamine oxide. Therefore, the coordination of trimethylamine oxide to a metal atom will result in no appreciable change in the N-O bond nature.

Vibrations Associated with Metal-oxygen. The bands at about 270 cm^{-1} proper to the zinc

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complexes appear to be associated with Zn–O, not with halogen atoms, because both the $ZnBr_2$ and the ZnI_2 complexes have bands at the same frequency and generally the zinc-bromine stretching frequencies of $ZnBr_4^{2-}$ or $ZnBr_2$ complexes are present in a lower frequency region.[15,16]

The band near 550 cm^{-1} appeared in a clear region of the ligand bands. On closer examination, these bands show slight but regular variations in positions according to the species of complexes. Rodley *et al.* proposed the assignment[11] to a metal-oxygen stretching vibration, ν(M–O). Although this possibility of assignment cannot be ruled out for the present case, a value of 550 cm^{-1} for ν(M–O) seems too high. Therefore, we adopt the assignment to the ligand vibration as mentioned in the foregoing section.

For a definite discussion of the origin and nature of the bands near 550 cm^{-1} and near 270 cm^{-1}, it is desirable to obtain other lower frequency bands below 250 cm^{-1}. Toward this end, far infrared studies are now in progress.

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