The Preparation of Trimethylamine Oxide Complexes and Some Infrared Studies

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Metal complexes of pyridine *N*-oxide have been prepared, and their infrared studies have been recently reported[1-3]. In these investigations, it has been shown that pyridine *N*-oxide readily combines with various metal ions in organic solvents to form metal complexes, and that the infrared frequency of the N-O stretching vibration of pyridine *N*-oxide considerably shifts to lower frequencies upon coordination to metal ions (1265→1220~1200 cm^{-1}). This shift has been attributed to a change in the contribution of the various resonance structures of pyridine *N*-oxide as a result of the coordination. In other words, the N-O stretching vibration shifts to a lower frequency, as the double bond character of the N-O bond decreases upon coordination A considerable difference in the behavior of the N-O stretching vibration would be expected in the case of trimethylamine oxide, since its N-O bond has no double-bond character. Infrared and Raman studies of trimethylamine oxide have been reported[4-8];

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[1] J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree, *J. Am. Chem.. Soc.*, **83**, 3770 (1961).

[2] S. Kida, J. V. Quagliano, J. A. Walmsley and S. Y. Tyree, *Spectrochimica Acta*, **19**, 189 (1963).

[3] Y. Kakiuti, S. Kida and J. V. Quagliano, ibid., **19**, 201 (1963).

[4] J. Goubeau and I. Fromme, *Z. anorg. u. allgem. Chem.*, **258**, 18 (1949).

[5] J. T. Edsall, *J. Chem. Phys.*, **5**, 225 (1937).

[6] J. Wagner, *Z. physik. Chem.* **40B**, 36 (1938).

[7] R. Matis-Noel, R. Wolf and F. Gallais, *Compt. rend.*, **242**, 1873 (1956).

[8] A. Giguere and D. Chin, *Can. J. Chem.*, **39**, 1214 (1961).

however, no investigation of its metal complexes has yet been reported*.

In the present investigation, it was attempted to prepare the metal complexes of trimethylamine oxide by the procedure used in the case of pyridine *N*-oxide, but it was found difficult, with the exception of the cobalt(II) complex, to obtain pure crystals of the products. The zinc(II) and cadmium(II) complexes were prepared as pure crystals by careful dehydration of the starting materials, but other metal ions, such as iron(II), nickel(II), copper(II), aluminum(III), chromium(III) and iron(III), failed to give pure products.

Matis-Noel et al.7) measured the infrared spectra of trimethylamine oxide and its derivatives and assigned the strong band at 952 cm^{-1} to the N–O stretching vibration. This assignment was based only upon a comparison of the spectrum of trimethylamine oxide with those of its derivatives; it does not seem to be a definite assignment. In fact, in trimethylamine oxide the N–O stretching vibration may probably be coupled with the other mode of vibration. Hence, in the present investigation, the normal coordinate treatment has been carried out on trimethylamine oxide, and the discussion has been extended to the metal complexes.

While this work was in progress, Giguere and Chin8) published a paper on the infrared spectra of trimethylamine oxide and its hydrochloride. They assigned the 937 cm^{-1} and 945 cm^{-1} bands to the N–O and the N–C stretching vibrations respectively. However, it appears to the present author that these two bands are due to a splitting of what should appear as a single band in a free molecule. One should be aware of the fact that a single band observed in solution or in a gaseous state may sometimes split into a couple of bands in the solid state. In fact, the frequencies of these two bands are close together, and the present experiment shows that, in a bromoform solution, only one band can be observed in this region; no splitting has ever been observed, as is shown in Fig. 1. Also, no such splitting was observed in the Raman investigation4).

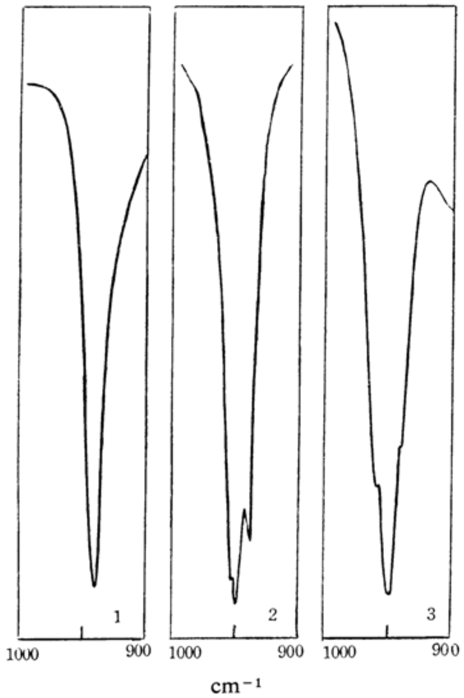

Fig. 1

1 ; Trimethylamine oxide in bromoform solution
2 : Trimethylamine oxide hydrochloride in KBr disk
3 : Trimethylamine oxide in KBr disk

Experimental

Preparation of the Compounds.—*Trimethylamine Oxide.*—The hydrate, $(CH_3)_3NO \cdot 2H_2O$, was first distilled under reduced pressure, then resublimed twice in vacuo.

Tetrakis (Trimethylamine Oxide) Cobalt(II) Nitrate.—To a solution of 2.0 g. of trimethylamine oxide in 10 ml. of 95% ethanol was added 1.0 g. of cobalt(II) nitrate hexahydrate dissolved in 10 ml. of 95% ethanol. The resulting deep blue-violet solution was evaporated to half volume and cooled in a refrigerator. The blue-violet crystals which were formed were collected on a glass filter, washed with ethanol, and dried in vacuo over phosphoric anhydride.

Found: C, 25.56; H, 6.46; Co, 10.62. Calcd. for $[Co\{(CH_3)_3NO\}_4](NO_3)_2$: C, 25.81; H, 6.50; Co, 10.56%.

Tetrakis (Trimethylamine Oxide) Cobalt(II) Perchlorate.—The compound was prepared as described for the corresponding nitrate from cobalt(II) perchlorate hexahydrate and trimethylamine oxide in ethanol. Deep blue-violet crystals were obtained. The compound melts at 207°C and explodes at 213°C.

Found: C, 25.56; H, 6.46; N, 10.30; Co, 10.62. Calcd. for $[Co\{(CH_3)_3NO\}_4](ClO_4)_2$: C, 25.81; H, 6.50; N, 10.34; Co, 10.56%.

Tetrakis (Trimethylamine Oxide) Zinc(II) Perchlorate.—Eight-tenth grams of zinc(II) perchlorate, previously dried over phosphoric anhydride in vacuo, was dissolved in 15 ml. of absolute ethanol. This solution was added to 1.7 g. of trimethylamine oxide dissolved in 15 ml. of absolute ethanol. The mixture was kept in a refrigerator overnight. The white fine crystals which were

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* Recently, the preparation of $CoBr_2L_2$ and $MnBr_2L_2$ (where L denotes trimethylamine oxide) has been reported: K. Isslied and A. Kreibich, *Z. anorg. u. allgem. Chem.*, **313**, 338 (1961).

precipitated were separated, washed with absolute ethanol, and desiccated over phosphoric anhydride. All these procedures were carried out in a dry box. The compound decomposes in the presence of moist air or moist solvents and melts at 210~230°C with decomposition.

Found: C, 25.13; H, 6.62; Zn, 11.29; Calcd. for $[Zn\{(CH_3)_3NO\}_4](ClO_4)_2$: C, 25.52; H, 6.62; Zn, 11.58%.

Tetrakis (Trimethylamine Oxide) Zinc(II) Nitrate.—This compound was prepared by the method described above for the corresponding perchlorate, using zinc(II) nitrate instead of zinc(II) perchlorate. The white crystals have properties similar to those of the corresponding nitrate and melt at 169°C with decomposition.

Found: C, 29.43; H, 7.21; Zn, 13.36. Calcd. for $[Zn\{(CH_3)_3NO\}_4](NO_3)_2$: C, 29.42; H, 7.41; Zn, 13.35%.

Tetrakis (Trimethylamine Oxide) Cadmium(II) Nitrate.—One gram of trimethylamine oxide was dissolved in 5 ml. of absolute methanol, and to this solution was added 0.45 g. of cadmium(II) nitrate which had been dried over phosphoric anhydride in vacuo and dissolved in 10 ml. of absolute methanol. The solvent was evaporated in an evacuated desiccator at room temperature. The resulting fine white crystals were collected on a glass funnel, washed with absolute ethanol, and desiccated over phosphoric anhydride. All these procedures were carried out in a dry box. M. p., 172°C.

Found: C, 26.53; H, 6.94; Cd, 20.89. Calcd. for $[Cd\{(CH_3)_3NO\}_4](NO_3)_2$: C, 26.85; H, 6.76; Zn, 20.94%.

Absorption Measurements.—The infrared spectra were obtained using a Perkin-Elmer infrared spectrophotometer model 221 equipped with a grating (4000~1400 cm^{-1}), an NaCl prism (1400~650 cm^{-1}), and a CsBr prism (680~300 cm^{-1}). All the spectra were obtained in Nujol mulls. The spectra in KBr disks were also obtained in the NaCl region and were checked against those in Nujol.

Calculation of Normal Vibrations

Considering the methyl group to be a dynamic unit, the skeletal vibrations of trimethylamine oxide have been treated as those of a five-body model of the point group C_{3v}.

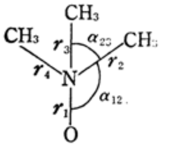
The secular equation was set up according to Wilson's[9] procedure, using a potential function of the Urey-Bradley type[10,11].

The symmetry coordinates for this calculation are the following:

$$\mathrm{A_1}\quad \begin{aligned} S_1 &= \Delta r_1 \\ S_2 &= 1/\sqrt{3}\cdot\Delta(r_2+r_3+r_4) \\ S_3 &= 1/\sqrt{6}\cdot\Delta(\alpha_{12}+\alpha_{13}+\alpha_{14} \\ &\qquad -\alpha_{34}-\alpha_{42}-\alpha_{23}) \end{aligned}$$

$$\mathrm{E}\quad \begin{aligned} S_{4a} &= 1/\sqrt{6}\cdot\Delta(2r_2-r_3-r_4) \\ S_{5a} &= 1/\sqrt{6}\cdot\Delta(2\alpha_{12}-\alpha_{13}-\alpha_{14}) \\ S_{6a} &= 1/\sqrt{6}\cdot\Delta(2\alpha_{34}-\alpha_{42}-\alpha_{23}) \end{aligned}$$

$$\mathrm{E}\quad \begin{aligned} S_{4b} &= 1/\sqrt{2}\cdot\Delta(r_3-r_4) \\ S_{5b} &= 1/\sqrt{2}\cdot\Delta(\alpha_{13}-\alpha_{14}) \\ S_{6b} &= 1/\sqrt{2}\cdot\Delta(\alpha_{42}-\alpha_{23}) \end{aligned}$$



The bond angles are regarded as tetrahedral, 109°28′. For the bond length, the values $r_{NO}=1.44$ and $r_{NC}=1.49$ Å, were used according to Rundle[12]. The force constants and intermolecular tension, κ, used in the calculation are shown in Table I. The values of F', the linear term of the interaction between non-bonded atoms, were determined using the relation, $F'=-1/10\cdot F$[13].

TABLE I. FORCE CONSTANTS IN 10^5 dyn./cm. AND INTERMOLECULAR TENSION IN 10^{-11} dyn. cm. OF TRIMETHYLAMINE OXIDE

	K		H		F	κ
N-O	2.30	O-N-CH_3	0.30	O···CH_3	0.80	0.05
N-CH_3	3.40	CH_3-N-CH_3	0.40	CH_3···CH_3	0.35	

Results and Discussion

The observed infrared frequencies are shown in Table II. They coincide with Giguere and Chins' values within the range of minimum experimental error. The assignment of the bands of the methyl group can be made as shown in the table according to the commonly accepted group frequencies of the methyl group[14]. Regarding the symmetry of the trimethylamine oxide molecule as a point group C_{3v}, there should be 3 non-degenerate vibrations in A_1 and 3 degenerate vibrations in E. Using the force constant values listed in Table I, we have obtained the results shown in Table III, in which each calculated frequency is related to the observed value. The values in Table I have been selected to produce the best agreement between the observed and calculated frequencies, but they also seem to be reasonable if compared with the values used in the calculation of trimethylamine[15] and tetramethylammonium ion[5] ($K=3.63$, $H=0.459$, $F=0.615$, for the former and $K=2.18$, $H=0.43$,

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[9] E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939).

[10] H. C. Urey and C. A. Bradley, *Phys. Rev.*, **38**, 1963 (1931).

[11] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

[12] R. E. Rundle, private communication quoted by P. W. Allen and L. E. Sutton in *Acta Cryst.*, **3**, 46 (1950).

[13] T. Shimanouchi, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **74**, 266 (1953).

[14] For instance, L. J. Bellamy, "Infrared Spectra of Complex Molecules", 2nd Ed., Methuen, London, (1958); K. Nakanishi, "Infrared Absorption Spectra", Nankodo, Tokyo (1960).

[15] K. Shimizu, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **77**, 1103 (1956).

TABLE II. OBSERVED INFRARED FREQUENCIES (cm^{-1}) OF TRIMETHYLAMINE OXIDE, THE HYDROCHLORIDE AND THE METAL COMPLEXES

Trimethylamine oxide (=L)		Hydrochloride	[Co L_4]-(ClO_4)$_2$	[Zn L_4]-(ClO_4)$_2$	[Zn L_4]-(NO_3)$_2$	[Cd L_4]-(NO_3)$_2$	
**	in $CHBr_3$	*	**	**	*	*	Assignment
1465 s	1470 s	1465 s	1490 s	1490 sh	1490 s	1479 sh	CH_3 deg. def.
	1451 s	1450 s	1470 s	1470 s	1470 s		
1400 m	1395 m	1429 m	1395 m	1395 m	1365 vs, b	1365 vs, b	CH_3 sym. def.
					(NO_3^-)	(NO_3^-)	
1245 s	—1)	1259 s	1240 m	1245 s	1245 m	1245 m	CH_3 rock.
1125 m	—1)	1124 m			1121 w	1127 m	C–N str. (E)
			1090 vs	1090 vs			
			(ClO_4^-)	(ClO_4^-)			
960 vw, sh		953 vw, sh					
948 s	940 s	948 s	947 sh	963 s	960 s	950 s	N–O str. (A_1)
941 w,		939 w	940 s	958 s	950 sh		
892 m, b						894 m, b	
865 m, b							
					827 m	835 m	
					(NO_3^-)	(NO_3^-)	
755 s	757 s	750 vs	765 s	770 s	770 s	757 s	C–N str. and N–O str. (A_1)
623 s, b	—1)	—3)	621 s	621 s	—3)	—3)	
	—1)	—3)	(ClO_4^-)	(ClO_4^-)	—3)	—3)	
509 m	536 m2)	—3)	563 s	560 s	—3)	—3)	C–N–O def. (E)
491 m	492 m	—3)					
464 s	457 m	—3)	480 s	478 s	—3)	—3)	C–N–O def. and C–N–C def. (A_1)
383 s	379 s	—3)	405 m	402 m	—3)	—3)	C–N–C def. (E)
		—3)	382 m	382 m	—3)	—3)	

* In KBr

** In KBr 1500~650 cm^{-1} and in Nujol 650~300 cm^{-1}

1) Strong solvent absorption

2) Obscure due to the solvent absorption

3) No good spectrum was obtained.

Abbreviations: L=trimethylamine oxide; s=strong; m=medium; w=weak; sh=shoulder; v=very

TABLE III. THE OBSERVED AND THE CALCULATED FREQUENCIES (cm^{-1}) OF THE SKELETAL VIBRATIONS OF TRIMETHYLAMINE OXIDE

Symmetry class	Raman4)	IRa)	Calcd.	Vibrational mode (c/o Table IV)
	945	948	961	N–O str.
A_1	759	755	771	N–CH_3 str. and N–O str.
	439	464	504	CH_3–N–O def. and CH_3–N–CH_3 def.
	1135	1125	1076	N–CH_3 str.
E	494	509 491	528	CH_3–N–O def.
	304	383	431	CH_3–N–CH_3 def.

a) In KBr 1500~650 cm^{-1} and in Nujol 650~300 cm^{-1}

$F=0.35$, for the latter), considering that the nature of the C–N bond of trimethylamine oxide is intermediate between those of these compounds. Furthermore, no alternative assignments of the vibrations which have been tried so far have given reasonable results. Goubeau and Fromme4) had calculated the frequencies of trimethylamine oxide using the central force field and had related each calculated frequency to the observed one, although the agreement between the calculated and the observed frequencies were poor compared with that of the present calculculations. Though the present assignment was carried out independently from that of Goubeau and Fromme, the results do not conflict with their results. Thus, the author believes these assignments to be correct.

The assignments of the skeletal vibrations shown in Table III are based on the results of the calculation of the potential energy distributions shown in Table V. The assignment of the band around 950 cm^{-1} does not conflict with that of Matis-Noel et al.7), in

TABLE IV. POTENTIAL ENERGY DISTRIBUTIONS AMONG SYMMETRY COODINATES $(F_{ii}L^2_{i\lambda})$

		ν_1	ν_2	ν_3
	S_1	0.3518	0.1434	0.0121
A_1	S_2	0.2685	0.1493	0.0203
	S_3	0.1956	0.0030	0.1063
		ν_4	ν_5	ν_6
	S_4	0.6493	0.0142	0.0021
E	S_5	0.0926	0.0911	0.0393
	S_6	0.0865	0.0362	0.0727

TABLE V. ***J***-Matrices $\{\partial\nu/\partial K$ etc.; $\nu(\text{cm}^{-1})$, K $(10^5$ dyn.$\cdot$cm$^{-1})\}$

A_1

	ν_1	ν_2	ν_3
K_{NO}	82	42	5
K_{NC}	49	34	7
H_{ONC}	141	3	145
H_{CNC}	146	3	150

E

	ν_4	ν_5	ν_6
K_{NC}	125	58	62
H_{ONC}	4	116	55
H_{CNC}	0.6	62	128

which the N–O stretching vibration mainly contributes to this band. However, Table IV shows that the N–C stretching and the deformation vibrations also considerably contribute to it. It has also been found that the N–O and the N–C stretching vibrations almost equally contribute to the band at 755 cm^{-1}. In the band at 1125 cm^{-1} a coupling with the deformation vibrations of the methyl group is possible to some degree, although in the present calculation this effect was not taken into consideration.

As may be seen in Table II, the vibrations of trimethylamine oxide do not shift much in the sodium chloride region upon coordination to metal ions. It is notable that the band at ~950 cm^{-1}, which is mainly contributed by the N–O stretching vibration, shows very little shift to the low frequency region. This makes a remarkable contrast to the relatively large shift in the N–O stretching vibration of pyridine *N*-oxide.

The very small shift of the N–O stretching vibration on coordination may be explained as follows: 1) The coordination effect is small because of the weak covalent character of the O-metal bond; 2) unlike pyridine *N*-oxide, trimethylamine oxide can not form π-bonding, and 3) this vibration is affected not only by the force constant K_{NO}, but also by K_{NC}, H_{CNC} and H_{CNO}. Therefore, even if K_{NO} is changed on coordination, the frequency shift of this band could considerably be canceled by the simultaneous change of the other force constants (as is understandable by looking at the ***J***-matrix in Table IV). It is not certain at the present stage which of these factors is mainly responsible for the observed spectral behavior.

The skeletal deformation vibrations appear in the cesium bromide region. As is shown in Table II, these bands undergo a large change upon coordination. This may be due to 1) a change in the character of the N–O bond due to the formation of the O-metal bond, or 2) a change in the steric arrangement of the surrounding groups. However, the latter reason seems more plausible to the author, since not only the frequencies but also the contour of the splitting changes upon coordination. However, further investigation is necessary to reach a definite conclusion on this point.

In the pyridine *N*-oxide complexes of cobalt(II) and zinc(II), the O-metal stretching vibration was observed in the 319~331 cm^{-1} region³⁾. In the present investigation, however, no crresponding band was found. It is possible that the band appears in a lower frequency region, below 300 cm^{-1}. One may, therefore, assume that the metal-O bonding of trimethylamine oxide complexes has a less covalent character than that of pyridine *N*-oxide complexes.

In addition to the bands mentioned above, broad bands were observed at 892 and 865 cm^{-1}, while a rather intense broad absorption appeared at 623 cm^{-1}. No fundamental vibrations could be assigned to these bands. In the Raman spectrum⁴⁾ no corresponding Raman lines were observed; all normal vibrations belonging to A_1 and E are infrared and Raman active in C_{3v} symmetry. They appear to be absorptions specific of the solid state (probably containing water), but no final conclusion can be drawn at present.

Summary

Metal complexes of trimethylamine oxide with cobalt(II), zinc(II) and cadmium(II) have been prepared.

The infrared spectra of trimethylamine oxide and its complexes have been measured in the 1500 to 300 cm^{-1} range. Assignment of the observed bands has been made on the basis of the calculation of the normal vibrations of trimethylamine oxide.

The band at 950 cm^{-1} was found to be mainly contributed by the N–O stretching vibration, as was expected from the former investigations, but it was also considerably contributed to by the other mode of vibrations.

The metal-O stretching band was not found in the region of the present investigation; consequently, a rather weak bond was assumed to exist between trimethylamine oxide and metal ions.

The experiments of this investigation were carried out in the Department of Chemistry, Florida State University. The author wishes to express sincere thanks to Professor J. V. Quagliano of the Florida State University for his kind help and valuable suggestions throughout this work. He also wishes to thank to Professor Yuzo Kakiuti of Rikkyo St. Paul's University for his helpful advice and discussion.

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