

DONOR-ACCEPTOR COMPLEXES OF TRIMETHYLAMINE WITH SELENIUM TRIOXIDE, SULPHUR TRIOXIDE, AND SULPHUR DIOXIDE

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Dedicated to Professor K. Dostál, on the occasion of his 60th birthday.

Study of reaction course of trimethylamine with selenium trioxide by conductometric titration and vibration spectra of the products proved that the reaction produces, besides the known donor-acceptor complex $(\text{CH}_3)_3\text{N} \cdot \text{SeO}_3$, also the adduct $(\text{CH}_3)_3\text{N} \cdot \text{S}_2\text{O}_6$ similar to that formed in the system pyridine-selenium trioxide. Although the latter adduct could not be isolated in pure state, the results obtained indicate its structural analogy to the compound $\text{C}_5\text{H}_5\text{N} \cdot \text{Se}_2\text{O}_6$. In preparation of the both DA complexes of selenium trioxide and trimethylamine the adduct $(\text{CH}_3)_3\text{N} \cdot \text{SO}_2$ is an important intermediate whose vibration spectra were measured and interpreted, too. Comparison and characterization of bonding relations in the DA complexes $(\text{CH}_3)_3\text{N} \cdot \text{SeO}_3$ and $(\text{CH}_3)_3\text{N} \cdot \text{SO}_3$ were carried out on the basis of results of normal coordinate analysis.

The complex $\text{TMA} \cdot \text{SeO}_3$ (TMA = trimethylamine) was prepared by reaction¹ of TMA with the adduct $\text{C}_5\text{H}_5\text{N} \cdot \text{SeO}_3$ and also by thermal decomposition² of the compound $\text{TMA} \cdot \text{O}_2\text{Se}[\text{OSi}(\text{CH}_3)_3]_2$. Although the donor-acceptor interaction in $\text{TMA} \cdot \text{SeO}_3$ is obviously greater than that in $\text{C}_5\text{H}_5\text{N} \cdot \text{SeO}_3$ due to greater basicity of TMA, the adduct $\text{TMA} \cdot \text{SeO}_3$ is a substantially more labile compound, being decomposed by mere standing at room temperature for several hours². Study of infrared spectra showed³ that both $\text{TMA} \cdot \text{SeO}_3$ and $\text{C}_5\text{H}_5\text{N} \cdot \text{SeO}_3$ are formed by monomer molecules and not by tetramers, which was incorrectly presumed earlier^{1,4}. We have tried to elucidate the reaction course of TMA with selenium trioxide by means of conductometric titration and vibration spectra of the products formed in the same way as earlier in the case of reaction of pyridine with selenium trioxide⁵.

Preparation of the DA complexes of selenium trioxide with TMA involves the adduct $\text{TMA} \cdot \text{SO}_2$ as an intermediate whose structure was followed predominantly by means of electronic spectra⁶⁻⁹. The Raman spectrum of $\text{TMA} \cdot \text{SO}_2$ was also measured¹⁰, but the position of the band due to vibration of the donor-acceptor bond SN was only discussed. Therefore, we also tried to discuss in more detail the interpretation of vibration spectra of this compound.

The final part of this paper deals with normal coordinate analysis of the molecules $\text{TMA}.\text{SeO}_3$ and $\text{TMA}.\text{SO}_3$ with the aim of verification of the values of quadratic potential constants published¹¹ for $\text{TMA}.\text{SO}_3$ and comparison of bonding relations in the two complexes on the basis of these values.

EXPERIMENTAL

Reagents. Selenium trioxide was prepared by dehydration of anhydrous selenic acid with diphosphorus pentoxide¹² and purified by vacuum distillation. TMA was dried by passing over solid potassium hydroxide and sodium wire and purified by distillation. Sulphur trioxide was obtained by distillation from 20% oleum and purified by distillation. The used solvents were purified and dried by usual methods.

Analytical methods. The hexavalent selenium was determined titrimetrically¹³. TMA was displaced from the samples by 30% potassium hydroxide solution and distilled into a known amount of 0.1M hydrochloric acid the excess of which was retitrated with 0.1M sodium hydroxide. The tetravalent sulphur was determined iodometrically, the hexavalent sulphur was determined gravimetrically as barium sulphate.

The procedure used for the conductometric titration is described in ref.¹⁴, the methods of determination of melting point, measurement of infrared and Raman spectra, and study of thermal behaviour are described in ref.⁵.

Preparation of $\text{TMA}.\text{SO}_2$. Gaseous TMA (8 g) was introduced slowly into 50 ml strongly cooled liquid sulphur dioxide to give a light yellow solution. Evaporation of excess sulphur dioxide gave a white crystalline precipitate which was rid of the rest of free sulphur dioxide in vacuum at room temperature. Melting point of this hygroscopic substance is 74–75°C, its yield was almost quantitative. For $\text{TMA}.\text{SO}_2$ (123.2) calculated: 47.99% TMA, 26.03% S; found: 48.04% TMA, 25.79% S.

Preparation of $\text{TMA}.\text{SeO}_3$. 2.1 g selenium trioxide was suspended in 50 ml liquid sulphur dioxide at -50°C , and 1.95 g $\text{TMA}.\text{SO}_2$ was added thereto portionwise. After several minutes stirring all the selenium dioxide dissolved, and a clear colourless solution was formed. On evaporation of the solvent in vacuum at about -15°C a white fine crystalline strongly hygroscopic solid separated which was rid of the rest of solvent in vacuum at room temperature. Yield fast quantitative; m.p. 122–124°C with decomposition. For $\text{TMA}.\text{SeO}_3$ (186.1) calculated: 42.44% Se, 31.77% TMA; found: 42.60% Se, 31.59% TMA.

Attempts of preparation of $\text{TMA}.\text{Se}_2\text{O}_6$. 2.2 g selenium trioxide was suspended in 80 ml liquid sulphur dioxide at -30°C , and the suspension obtained was treated portionswise with 1.07 g $\text{TMA}.\text{SO}_2$. After several minutes stirring a clear solution was formed which became turbid (white turbidity) on slow heating to -20°C . After several minutes the reaction mixture separated into two liquid phases: the upper one formed by the solvent used and the lower one formed by the saturated solution of sulphur dioxide in $\text{TMA}.\text{Se}_2\text{O}_6$. After removal of the upper layer of sulphur dioxide in vacuum the lower liquid phase began to separate a solid. Last remainders of sulphur dioxide could not be removed even in vacuum at 40°C . The obtained very hygroscopical product was not homogeneous and could not be characterized analytically due to its consistency.

Preparation of $\text{TMA}.\text{SO}_3$. Vacuum sublimation of the product prepared by reaction of $\text{TMA}.\text{SO}_2$ with sulphur trioxide in liquid sulphur dioxide medium¹⁵ gave the product in the form of long needles (up to several cm). Its melting point agreed with refs^{16,17} (240°C). For $\text{TMA}.\text{SO}_3$ (139.2) calculated: 42.47% TMA, 57.53% SO_3 ; found: 42.39% TMA, 57.92% SO_3 .

RESULTS AND DISCUSSION

Vibration Spectra and Thermal Behaviour of TMA.SO₂

If the stereochemical activity of the free electron pair at tetravalent sulphur atom is considered, then a single space configuration of the TMA.SO₂ molecule is possible with the SO₂ group located in a plane perpendicular to the symmetry plane of the molecule. It belongs to the C_s point group and is characterized by the following fully reduced vibration representation

$$\Gamma = 23A''^{P,\alpha} + 19A''^{P,\alpha}.$$

The vibration spectra of TMA.SO₂ are given in Table I. For their interpretation we used the data of refs^{18,19} concerning the assignment of vibration spectra of tri-

TABLE I
Vibration spectra of TMA.SO₂^a

RA, s		RA, in SO ₂		IR, s		Assignment
$\tilde{\nu}$, cm ⁻¹	<i>I</i>	$\tilde{\nu}$, cm ⁻¹	<i>I</i>	$\tilde{\nu}$, cm ⁻¹	<i>I</i>	
167	vw					} τ_{SN} ρ , $\rho'NC_3$, τ_sCH_3
202	vs	203 p	vs			
267 Sh	vw	275	vw			
294	w	297 p	w			} τ'_s , $\tau_{as}CH_3$ ωSO_2 , δ'_sNC_3
383	vw	386 dp	vw			
433	m	435	w			} ρSO_2 δ'_sNC_3 $\delta_{as}NC_3$
453	s	455 p	s	465 b	s	
473	m					
555	vw	555 p	vw	556	s	δSO_2
798	m	796 p	w	795	s	ν_sNC_3
1 018	vw	1 020	vw	1 018	s	ν'_s , $\nu_{as}NC_3$
1 088	vs	1 091 p	vs			} ν_sSO_2 ρ_eCH_3
1 103	m	1 100 Sh	s	1 098	vs	
1 224	s	1 221 p	m	1 220	s	ρ_sCH_3
1 276	vw	1 274	vw	1 272	m	$\nu_{as}SO_2$
1 300	vw	1 300 Sh	vw	1 300 Sh	w	ρ'_eCH_3
1 413	vw	1 414	vw	1 404	w	} $\delta_{s+as}CH_3$
1 448	w	1 451	vw	1 457 Sh	m	
1 475	vw	1 474 Sh	vw	1 473 b	m	
1 488	vw					

^a The intensities are denoted as follows: vw very weak, w weak, m medium, s strong, vs very strong band; Sh partially overlapped band (shoulder), b broad band; p polarized, dp depolarized band.

methylamine which was also supported by normal coordinate analysis¹⁹. The interpretation given in the Table V for valence vibration bands of SO and CN bonds is beyond a doubt. Identification of the band due to valence vibration of the coordination bond SN is more difficult. Hata and Kinumaki¹⁰ presume that this vibration is connected with a strong band at 186 cm^{-1} in the Raman spectrum. In the spectrum obtained by us for solid $\text{TMA}\cdot\text{SO}_2$ we observed in this region a weak band at 167 cm^{-1} and a strong band (polarized in the spectrum of the solution) at 202 cm^{-1} . In the range of 500 to 400 cm^{-1} three partially overlapped bands were found altogether, two of which with higher wave numbers (473 and 453 cm^{-1}) coalesce in the spectrum into a single strong polarized band ($q = 0.27$). From comparison of wave numbers of fundamental vibrations of NC_3 skeleton in TMA and some complexes of this base²⁰⁻²³ (which, according to the findings by Kurze and Paetzold³, represents a good measure of magnitude of the donor-acceptor interaction) it can be inferred that magnitude of charge transfer in $\text{TMA}\cdot\text{SO}_2$ is relatively considerable, and the band due to valence vibration of SN should rather lie in the higher of the two discussed regions. In our opinion it is probable that the bands at 167 and 202 cm^{-1} , belong to deformation vibrations of the molecule, the valence vibration SN being connected with only one of the bands at 453 and 473 cm^{-1} .

Study of thermal behaviour of $\text{TMA}\cdot\text{SO}_2$ showed that there are two marked endothermic effects at the DTA curve. One of them corresponds to the melting point (at 75°C) and the other (at about 114°C) to decomposition of the complex into its components which escape quantitatively in gaseous form.

Conductometric Titration of TMA-Selenium Trioxide System

The titration curve of the studied system is given in Fig. 1. The first additions of $\text{TMA}\cdot\text{SO}_2$ cause the conductivity to increase to a maximum value at the molar

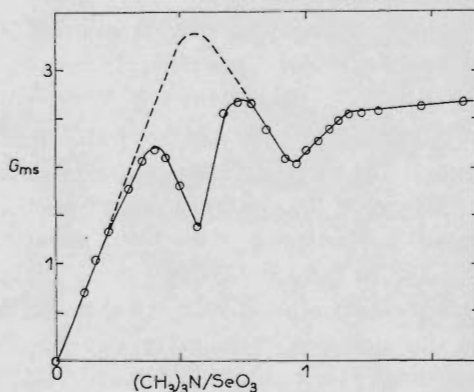


FIG. 1

Titration curve of the system trimethylamine-selenium trioxide ($1.35\text{ g (SeO}_3)_4$ in 140 ml liquid sulphur dioxide)

ratio about 1 : 3. From this point on the conductivity decreases to a minimum at the molar ratio about 1 : 2. This section of the titration curve corresponds to formation of the complex $\text{TMA} \cdot \text{Se}_2\text{O}_6$ the solubility of which in liquid sulphur dioxide is limited; on exceeding a certain concentration it begins to separate from the solution in the form of heavy oily liquid, which results in the observed conductivity decrease. If $\text{TMA} \cdot \text{Se}_2\text{O}_6$ were not separated from the solution, the curve would have monotonous increasing character in the discussed section with the maximum at the molar ratio 1 : 2, as it is seen in Fig. 1 (dashed line), and it would be quite analogous to the titration curve of the system pyridone–selenium trioxide²⁴. Reaching of the molar ratio 1 : 1 again is characterized by a minimum at the titration curve. At the molar ratio about 1.1 : 1 the curve shows a break corresponding to the moment when a redox reaction proceeds in the system due to excess of TMA, which makes itself felt by the reaction mixture turning slightly red due to reduction of hexavalent selenium down to elementary selenium.

Vibration Spectra and Structure of $\text{TMA} \cdot \text{SeO}_3$ and $\text{TMA} \cdot \text{Se}_2\text{O}_6$

The RA spectra of $\text{TMA} \cdot \text{SeO}_3$ given in Table II fully confirm the conclusion by Kurze and Paetzold³ made on the basis of study of IR spectra, *viz.* that the compound is formed by monomer molecules with C_{3v} symmetry. Its fully reduced vibration representation has the following form:

$$\Gamma = 10A_1^{P,\alpha} + 5A_2^- + 15E^{P,\alpha}.$$

The interpretation of vibration spectra of $\text{TMA} \cdot \text{SeO}_3$ given in Table II is (except for several points) identical with data of ref.³. The bands about 980 and 960 cm^{-1} are assigned³ to the degenerated valence vibrations of the bonds SeO and CN, respectively. The latter band is split in RA spectrum, whereas the former one is not. Splitting of the band due to $\nu_e(\text{NC}_3)$ has not yet been observed in any spectrum of the TMA complexes studied, whereas the splitting of the band due to $\nu_e(\text{SeO}_3)$ is very frequent in spectra of solid samples. Hence we judge that the reverse assignment of these bands is more likely, which is confirmed by results of normal coordinate analysis.

In the region 550–400 cm^{-1} the spectra of $\text{TMA} \cdot \text{SeO}_3$ show three bands altogether. The most intensive of them, which in RA spectrum of the solid sample lies at 531 cm^{-1} , belongs obviously to valence vibration of the bond SeN. By this band partially overlapped is the band about 520 cm^{-1} which is interpreted as $\delta_e(\text{NC}_3)$ in ref.³, the band at 435 cm^{-1} being interpreted as $\delta_s(\text{NC}_3)$. However, from polarization measurements it followed that the last of the given bands is depolarized and, in our opinion, belongs to two degenerated vibrations $\delta_e(\text{SeO}_3)$ and $\delta_e(\text{NC}_3)$. Splitting of the band about 530 cm^{-1} into two components results obviously from the presence of more than one $\text{TMA} \cdot \text{SeO}_3$ molecule in the elementary cell of the crystal.

TABLE II
Vibration spectra of TMA.SeO₃ and Raman spectrum of TMA.Se₂O₆^a

TMA.SeO ₃				TMA.Se ₂ O ₆ ^b				Assignment
IR, s ^d		RA, s		RA, in SO ₂		RA, in SO ₂		
$\tilde{\nu}$, cm ⁻¹	<i>I</i>	$\tilde{\nu}$, cm ⁻¹	<i>I</i>	$\tilde{\nu}$, cm ⁻¹	<i>I</i>	$\tilde{\nu}$, cm ⁻¹	<i>I</i>	
		78	vw					} $\delta_{\text{latt.}}$
		115	vw					
		149	vw					
		168	vw					
		197	m	201 dp	w	206	m	
		228	vw	228 Sh	vw	227 Sh	m	$\rho_e\text{CH}_3$
						238 Sh	m	δSeOSe^c , $\rho, \rho_e\text{SeO}_2\text{N}^c$
		260	vs	258 p	s	261	s	$\delta_s\text{NC}_3$
		292	m	298 dp	w	299	m	$\rho_e\text{SeO}_3, \delta_s\text{NSeO}^c$
		364	m	367 p	w	370	w	$\delta_s\text{SeO}_3, \delta\text{SeO}_2^c$
		378	vw			404	vw	} $\delta_e\text{SeO}_3, \delta_e\text{NC}_3$
432	m	435	w	433 dp	vw	435	w	
515 Sh	w	520 Sh	vw			505 Sh	w	} νSeN
530	vs	531	m	527 p	m	530	m	
						558 Sh	w	$\nu_a\text{SeOSe}^c$
						672 Sh, b	vw	
						739 b	w	$\nu_{\text{as}}, \text{SeOSe}^c$
785	s	785	w	787 p	w	785	w	$\nu_s\text{NC}_3$
		825	vw	825 p	vw	824	vw	?
872	s	873	vs	874 p	vs	884	vs	$\nu_e\text{SeO}_3$
		949	m					} $\nu_e\text{SeO}_3$
960	m	965	w	961 dp	w	947	s	
980	s	982	w	981 dp	vw	984	vw	$\nu_e\text{NC}_3$
						1 023	w	$\nu_{\text{as}}\text{SeO}_2^c$
1 111	m	1 111	vw	1 113 Sh	vw	1 113	vw	$\rho_e\text{CH}_3$
1 238	m	1 243	m	1 247 p	w	1 251	w	$\rho_s\text{CH}_3$
1 259	m	?		?		?		$\rho'_e\text{CH}_3$
1 410	s	1 417	vw	1 421	vw	1 426 Sh	vw	} $\delta_{s+e}\text{CH}_3$
1 455	s	1 453	vw	1 436	vw	1 438	vw	
1 470	s	1 463	vw	1 458	w	1 457	vw	
1 484	s	1 481	w	1 470	vw	1 472 Sh	vw	

^a The intensities are denoted as in Table I. ^b The sample for the measurement contained still SO₂ (wave numbers of its normal vibrations are not given in this Table). ^c It only corresponds to TMA.Se₂O₆. ^d See ref.³.

On the basis of the polarization measurement it was necessary also to change the interpretation³ of the bands due to the vibrations $\rho(\text{CH}_3)$. The band at 1257 cm^{-1} is polarized and, therefore, must belong to $\rho_s(\text{CH}_3)$. Out of the two expected bands for $\rho_e(\text{CH}_3)$ one was only found in RA spectrum at 1114 cm^{-1} . The other with wave number 1259 cm^{-1} was observed in IR spectrum only.

In the optimum case, molecule of the complex $\text{TMA}.\text{Se}_2\text{O}_6$ can belong to the C_s point group. However, polarization measurement with a liquid sample containing considerable amounts of sulphur dioxide showed that all the bands in RA spectrum are polarized, and $\text{TMA}.\text{Se}_2\text{O}_6$ has the trivial symmetry C_1 . The obtained spectrum is given in Table II wherefrom also follows its interpretation which agrees well with the data obtained⁵ from the vibration spectra of $\text{C}_5\text{H}_5\text{N}.\text{Se}_2\text{O}_6$. On the basis of these results it can be stated that courses of reactions of selenium trioxide with TMA and pyridine are analogous in principle, which was expected. The observed differences are due only to different physico-chemical properties of the formed compounds.

Raman Spectrum of TMA.SO₃

Table III gives RA spectrum of $\text{TMA}.\text{SO}_3$ along with the known¹¹ IR spectrum of this compound. The data confirm the interpretation of IR spectra given by Watari¹¹ to be justifiable. The band belonging to the vibration $\rho_e(\text{NC}_3)$ was not observed in the IR spectrum, although the measurement started from 80 cm^{-1} . In RA spectrum of solid $\text{TMA}.\text{SO}_3$ there are three weak bands in the region $300-150\text{ cm}^{-1}$, out of which two ones with higher wave number belong obviously to $\rho_e(\text{NC}_3)$ and $\tau_e(\text{CH}_3)$, and the third one belongs to some of the lattice vibrations. The bands at 220 and 259 cm^{-1} were assigned to $\rho_e(\text{NC}_3)$ and $\tau_e(\text{CH}_3)$. In RA spectrum of the solution these bands could not be observed due to their low intensity.

Normal Coordinate Analysis of TMA.SO₃ and TMA.SeO₃ Complexes

The model of the $\text{TMA}.\text{ZO}_3$ ($Z = \text{S}, \text{Se}$) complexes used for calculation of quadratic potential constants is given in Fig. 2. If CH_3 groups are taken as vibrating units with relative mass 15, then the following fully reduced vibration representation belongs to the $\text{TMA}.\text{ZO}_3$ molecules in C_{3v} point group:

$$\Gamma = 5A_1^{P,\alpha} + A_2^- + 6E^{P,\alpha}.$$

The torsion vibration $\tau(\text{ZN})$ belonging to the type A_2 is inactive in the both types of spectra. For the calculation we used the values of normal vibrations taken from RA spectra of the solutions in sulphur dioxide. Only when some band could not be identified in the spectrum of the solution due to its low intensity, the wave number was taken from RA spectrum of the solid sample.

TABLE III
Vibration spectra of TMA.SO₃^a

IR, s ^c $\tilde{\nu}$, cm ⁻¹	RA, s		RA, in SO ₂		Assignment
	$\tilde{\nu}$, cm ⁻¹	<i>I</i>	$\tilde{\nu}$, cm ⁻¹	<i>I</i>	
	161	vw			$\delta_{\text{latt.}}$
	220	vw			$\rho_e\text{NC}_3$
	259	vw			$\rho_e\text{CH}_3$
313	318	vs	312 p	m	$\delta_s\text{NC}_3$
353	354	m	350 dp	w	$\rho_e\text{SO}_3$
448	453	vw	446 dp	vw	$\delta_e\text{NC}_3$
540	543	s	540 p	m	$\delta_s\text{SO}_3$
560	567	vw	563 dp	w	$\delta_e\text{SO}_3$
622	618	m	628 p	w	νSN
799	804	w	803 p	m	$\nu_s\text{NC}_3$
973	977	vw	982 dp	vw	$\nu_e\text{NC}_3$
1 054	1 059	vs	1 061 p	vs	$\nu_s\text{SO}_3$
1 107	1 118	vw	?		$\rho_e\text{CH}_3$
1 251	1 248	w	^b		$\delta_s\text{CH}_3$
1 293	1 298	vw	^b		$\rho_e'\text{CH}_3$
1 310	1 327	vw	^b		
	1 413	vw			$\delta_{s+e}\text{CH}_3$
1 441	1 450	vw	1 459	w	
1 465	1 478	vw	1 472 Sh	vw	
1 484					

^a The intensities are denoted as in Table I. ^b Overlapped by bands of the solvent. ^c See ref.¹¹.

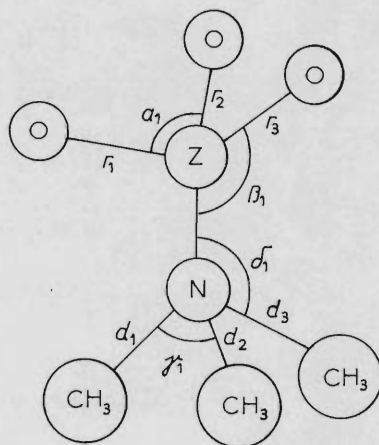


FIG. 2
Model of the TMA.ZO₃ molecules (Z = S, Se) which was used for normal coordinate analysis

Structural parameters of the both complexes were assessed on the basis of experimental values of cognate compounds – $r_{\text{SN}} = 162$ pm, $r_{\text{SeN}} = 166$ pm, $r_{\text{SO}} = 148$ pm, $r_{\text{SeO}} = 158$ pm, $r_{\text{CN}} = 155$ pm, the angle $\text{OZO} = 115^\circ$, $\text{OZN} = 110.9^\circ$. Calculation of the quadratic potential constants was carried out by the Wilson GF matrix method using a Tesla 200 computer and a set of programs described in refs^{25,26}. For transformation of the G and F matrices arranged in inner coordinates to the block diagonal form we used the following set of symmetrical coordinates:

$$S_1 = (\Delta r_1 + \Delta r_2 + \Delta r_3)/\sqrt{3}$$

$$S_2 = (\Delta d_1 + \Delta d_2 + \Delta d_3)/\sqrt{3}$$

$$S_3 = R$$

$$S_4 = N_1[r^{1/2}(\Delta\alpha_{23} + \Delta\alpha_{13} + \Delta\alpha_{12}) - R^{1/2}(\Delta\beta_1 + \Delta\beta_2 + \beta\Delta_3)]$$

$$S_5 = N_2[d^{1/2}(\Delta\gamma_{23} + \Delta\gamma_{13} + \Delta\gamma_{12}) - R^{1/2}(\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3)]$$

$$S_6 = N_1[R^{1/2}(\Delta\alpha_{23} + \Delta\alpha_{13} + \Delta\alpha_{12}) + r^{1/2}(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)]$$

$$S_7 = N_2[R^{1/2}(\Delta\gamma_{23} + \Delta\gamma_{13} + \Delta\gamma_{12}) + d^{1/2}(\Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3)]$$

for the block A_1 (N_1 and N_2 are the normalisation coefficients, S_6 and S_7 are the redundant coordinates) and

$$S_8 = (2\Delta r_1 - \Delta r_2 - \Delta r_3)/\sqrt{6}$$

$$S_9 = (2\Delta d_1 - \Delta d_2 - \Delta d_3)/\sqrt{6}$$

$$S_{10} = (2\Delta\alpha_{23} - \Delta\alpha_{13} - \Delta\alpha_{12})/\sqrt{6}$$

$$S_{11} = (2\Delta\gamma_{23} - \Delta\gamma_{13} - \Delta\gamma_{12})/\sqrt{6}$$

$$S_{12} = (2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)/\sqrt{6}$$

$$S_{13} = (2\Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3)/\sqrt{6}$$

or

$$S'_8 = (\Delta r_2 - \Delta r_3)/\sqrt{2}$$

$$S'_9 = (\Delta d_2 - \Delta d_3)/\sqrt{2}$$

$$S'_{10} = (\Delta\alpha_{13} - \Delta\alpha_{12})/\sqrt{2}$$

$$S'_{11} = (\Delta\gamma_{13} - \Delta\gamma_{12})/\sqrt{2}$$

$$S'_{12} = (\Delta\beta_2 - \Delta\beta_3)/\sqrt{2}$$

$$S'_{13} = (\Delta\delta_2 - \Delta\delta_3)/\sqrt{2}$$

for the blocks E .

In the diagonal valence force field approach used for calculation of the potential constants of the TMA.SO₃ molecule in ref.¹¹ the iteration process for the block A_1 of the both TMA.ZO₃ molecules gave physically meaningless solution presuming assignment of the band with the lowest wave number to valence vibration of the coordination bond ZN. Differences between the calculated and experimental values of wave numbers of the fundamental vibrations also were not negligible. The solu-

TABLE IV
Quadratic potential constants (QPC) in TMA.SO₃ and TMA.SeO₃ complexes

QPC ^{a, c}	TMA.SeO ₃ (N m ⁻¹)	TMA.SO ₃ (N m ⁻¹)
f_{ZO}	677.2	905.0
f'_{ZO}	8.7	26.5
f_{CN}	297.0	301.5
f'_{CN}	41.9	40.8
f'_{ZN}	259.5	309.6
f_{OZO}^b	55.68	82.24
f_{OZN}^b	42.88	52.89
f_{CNC}^b	58.68	58.18
f_{ZNC}^b	28.67	35.07
$f_{OZO/OZN}$	- 0.1	- 6.4
$f_{CNC/ZNC}$	1.5	- 1.7
F_{23}^{A1}	47.2	72.3
F_{34}^{A1}	-17.2	-50.9
F_{35}^{A1}	-49.9	-57.4
$F_{12}^E = F_{56}^E$	5.0	-
F_{34}^E	-	-10.0

^a The deformation and interaction potential constants are modified by means of the bond lengths including the corresponding angle so that their dimension size might be the same as that of the valence potential constants, *i.e.* N m⁻¹. ^b The fixed potential constants. ^c Z = S, Se.

tion obtained in the degenerated blocks E corresponded to the presumed interpretation, but full agreement between the calculated and the measured wave number values was not reached, either. Preliminary calculations showed that the wave number differences in the blocks E can be avoided by considering non-zero values for non-diagonal elements F_{12} and F_{56} (in the case of TMA.SeO₃) and F_{34} (in the case of TMA.SO₃). Due to lack of experimental data they had to be fixed in the calculations — the values 5 Nm^{-1} for F_{12} and F_{56} (TMA.SeO₃) and -10 Nm^{-1} for F_{34} (TMA.SO₃) enabled to reach complete agreement between the calculated and experimental values of wave numbers of the degenerated vibrations of the two complexes. As early as in this calculation phase it was possible to confirm justification of the interpretation of the band at 533 cm^{-1} in spectrum of TMA.SeO₃ to the both deformation vibrations $\delta_e(\text{SeO}_3)$ and $\delta_e(\text{NC}_3)$. The potential constant f_{CNC} obtained with this presumption was in good agreement with that calculated for the TMA.SO₃ molecule, whereas assignment of the partially overlapped band at 520 cm^{-1} to this vibration led to an almost double f_{CNC} value.

To obtain physically acceptable solution for the blocks A_1 it was necessary to introduce further non-diagonal element of the matrices F_s into the calculation. Preliminary calculations showed that the elements F_{23} , F_{34} , F_{35} and the interaction constants $f_{\text{OZO/OZN}}$ and $f_{\text{CNC/ZNC}}$ must be considered which are (provided $f_{\text{OZO/OZN}} = f'_{\text{OZO/OZN}}$ and $f_{\text{CNC/ZNC}} = f'_{\text{CNC/ZNC}}$) involved in the elements F_{44} and F_{55} , respectively, with high numerical coefficient. Therefore, in the final calculation we fixed the deformation potential constants f_{OZO} , f_{OZN} , f_{CNC} , and f_{ZNC} obtained by independent solution of the blocks E , which made it possible to adjust all the said elements of matrices $F_s^{A_1}$. Under these conditions the iteration process gave very well-consistent sets of quadratic potential constants for the two molecules TMA.ZO₃ (Table IV). Their introduction back into the secular equations made it possible to reproduce the experimental wave number values of fundamental vibrations with errors less than 1 cm^{-1} . Also the distribution of potential energy given in Table V agrees well with the expectation.

Neglecting of some (often important) interaction potential constants (e.g. f'_{OZO} , f'_{CNC} etc.), fixation of four deformation potential constants, and introduction of the condition $F_{12} = F_{56}$ for TMA.SeO₃ in the block E was inevitable due to limited number of experimental data. Therefore, the calculated values of the deformation and interaction quadratic potential constants considered in the calculations will obviously be loaded with a certain error. However, magnitude of the valence potential constants should not be significantly affected, which is documented by the following finding.

There is no qualitative difference between the SO and SeO bonds in structurally analogous compounds. Therefore, there exists a linear relation between their quadratic potential constants²⁷. The values calculated for f_{ZO} in the TMA.ZO₃ complexes fulfil this relation very well (with errors below 1%) and confirm thus complete struc-

tural analogy between the two compounds. The ZO bond order ($N_{SO} = 1.83$; $N_{SeO} = 1.58$ according to ref.²⁸) also agrees with their presumed multiplicity and somewhat different polarity.

The relatively high bond order of the coordination bonds ZN ($N_{ZN} \approx 0.8$) indicates a strong bonding interaction between the both components of the complexes and an almost equal sharing of electron pair by the atoms Z and N. Formation of DA bond affects the bonding relations predominantly in the donor section of the TMA. \cdot ZO₃ complexes. These changes are manifested by a relatively low value of the potential constant f_{CN} , which signals an enhanced polarity of CN bonds. If CH₃ group is considered to be a vibrating unit with relative mass 15 and if the wave number values²⁹ of normal vibrations ($\nu_s(\text{NC}_3)$ 826 cm⁻¹, $\nu_e(\text{NC}_3)$ 1 102 cm⁻¹, $\delta_s(\text{NC}_3)$ 364 cm⁻¹, and $\delta_e(\text{NC}_3)$ 422 cm⁻¹) are used, then the value 411 Nm⁻¹ is obtained for f_{CN} in TMA, *i.e.* by 1/3 higher than that in the two complexes. On the contrary, mutual interaction between CN bonds is markedly greater in TMA.ZO₃ (f'_{CN} about 41 Nm⁻¹) than in TMA ($f'_{CN} = 13$ Nm⁻¹). Hence it can be judged that the easy redox decomposition of TMA.SeO₃ is enabled by intermolecular interaction of the both strongly polar groups of this complex. A smaller tendency to redox decomposition observed⁵

TABLE V

Interpretation of vibration spectra of the TMA.ZO₃ complexes (Z = S, Se) inclusive of potential energy distribution

Symmetry type	No	Assign-ment	TMA. SeO ₃		TMA.SO ₃	
			$\tilde{\nu}$, cm ⁻¹	distribution of potential energy ^a , %	$\tilde{\nu}$, cm ⁻¹	distribution of potential energy ^a , %
<i>A</i> ₁	1	$\nu_s\text{ZO}_3$	874	99 ν_1	1 061	95 ν_1
	2	$\nu_s\text{CN}_3$	787	62 ν_2 + 21 ν_3	803	47 ν_2 + 28 ν_3 + 25 ν_5
	3	νZN	527	49 ν_3 + 34 ν_5	628	47 ν_3 + 28 ν_4
	4	$\delta_s\text{ZO}_3$	367	74 ν_4	540	20 ν_2 + 53 ν_4 + 26 ν_5
	5	$\delta_s\text{NC}_3$	258	25 ν_3 + 33 ν_4 + 42 ν_5	312	29 ν_3 + 20 ν_4 + 50 ν_5
<i>E</i>	6	$\nu_e\text{ZO}_3$	962	78 ν_6	1 312 ^b	90 ν_6
	7	$\nu_e\text{CN}_3$	981	52 ν_7	982	66 ν_7
	8	$\delta_e\text{ZO}_3$	433	85 ν_8	563	90 ν_8
	9	$\delta_e\text{NC}_3$	433	22 ν_7 + 64 ν_9	446	26 ν_7 + 65 ν_9
	10	ρZO_3	298	54 ν_{10} + 31 ν_{11}	350	49 ν_{10} + 23 ν_{11}
	11	ρNC_3	201	36 ν_{10} + 63 ν_{11}	200	33 ν_{10} + 66 ν_{11}

^a Only the contributions higher than 20% (rounded-off to integers) are given. ^b The average value of the wave numbers 1 298 and 1 327 cm⁻¹ taken from RA spectrum of the solid sample.

with $C_5H_5N.SeO_3$ is then obviously connected with aromatic character of pyridine ring the π electron system of which lowers electrophilic character of reaction centres at the carbon atoms bound immediately to the nitrogen atom of pyridine.

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