Spectrochemical Study of Microscopic Crystals. XIX[1] *The Structure and Absorption Spectra of Fremy's Salt*

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In the nineteenth century, Fremy[2] isolated an interesting compound having an empirical formula of $ON(SO_3)_2K_2$, which is violet-blue in solution and yellow in the crystalline state. This phenomenon, which has been studied by a number of investigators[3,4] was eventually understood on the assumption that the compound might consist of monomeric ions in solution and of dimeric ions in the crystalline state[5-7]. Aside from the electronic structure of the monomeric ion involving a queer type of bonding, the structure of the dimeric ion was often discussed by the earlier investigators, but still remains in dispute. Although the compound has been studied from various sides, no spectral data have so far been reported. In an attempt to elucidate the structure of Fremy's salt, we have carried out a spectroscopic study with this salt and related compounds.

Experimental

Materials. — Potassium peroxylamine disulfonate, $K_2(O_3S)_2NO$, was prepared by the method of Haga[8] with slight modification. To a solution of 17.5 g. of sodium nitrite in 50 ml. of water were added 100 g. of crushed ice, a solution of 25 g. of sodium hydrogen sulfite in 50 ml. of water under continuous stirring, and finally 10 ml. of glacial acetic acid. After a few minutes the reaction mixture was rendered alkaline by the addition of 7 ml. of concentrated aqueous ammonia (*d*, 0.880), and then a solution of 6.3 g. of potassium permanganate in 200 ml. of water was added under stirring. The precipitate of manganese dioxide which was at once formed was removed by filtration. To the violet-colored filtrate was added 250 ml. of a saturated solution of potassium chloride. Orange-yellow crystals which precipitated were filtered by suction, and washed successively with a 5% solution of potassium hydroxide, ethanol and acetone. Recrystallization from water yielded orange-yellow crystals of Fremy's salt, which showed the typical reactions of Fremy's salt. Thus the crystals were dissolved in water to give a blue-violet solution, from which the orange-yellow crystals separated again on concentration. Potassium peroxylamine disulfonate thus prepared was found to form blue-colored mixed crystals with potassium hydroxylamine disulfonate, which was prepared in colorless crystals according to the method of Rollefson and Oldershaw[8].

The mixed crystals were prepared in the following way. Into 45 ml. of a 5% solution of potassium hydroxide were added 1 g. of potassium hydroxylamine disulfonate and 0.5 g. of potassium peroxylamine disulfonate at 45°C. The solution was filtered and cooled with crushed ice. After twenty hours large mixed crystals which were blue in color began to separate together with the crystals of potassium peroxylamine disulfonate. The blue mixed crystals were picked up from the mixture mechanically. Accurate determination of the $K_2(O_3S)_2NO$ content in the mixed crystal was not made, but approximate estimation from the intensity of the "NO band" showed it to be only a few per cent. The value seems to agree well with those reported earlier[5].

Measurements.—Quantitative dichroism measurements in the visible and ultra-violet regions were carried out at room temperature by Tsuchida and Kobayashi's microscopic method[9].

Absorption spectra of the compounds in aqueous solution were determined at room temperature by a Beckman DU spectrophotometer.

Infrared absorption spectra of the compounds in Nujol mulls and in potassium bromide discs were determined in the rock salt region by a Hilger H 800 infrared spectrophotometer.

The notations in the present paper are the same as those used in the former papers of this series.

Results and Discussion

Visible and Ultra-violet Absorption Spectra.—The mixed crystal formed from $K_2(O_3S)_2NOH$ and $K_2(O_3S)_2NO$ shows an absorption band at 52×10^{13}/sec., as seen

1) Part XVIII of this series, S. Yamada and R. Tsuchida, This Bulletin, **31**, 813 (1958).
2) E. Fremy, *Ann. chim. phys.*, **15**, iii, 408 (1845).
3) F. Raschig, *Ann.*, **241**, 223 (1887).
4) A. Claus, ibid., **158**, 205 (1871).
5) A. Hantzsch and W. Semple, *Ber.*, **28**, 2744 (1895).
6) T. Haga, *J. College of Sci. Imp. Univ. Tokyo*, **19**, No. 15 (1904); T. Haga and E. Divers, *J. Chem. Soc.*, **77**, 440 (1900).
7) R. W. W. Asmussen, *Z. anor. allgem. Chem.*, **212**, 316 (1933).
8) T. Haga, *J. Chem. Soc.*, **85**, 78 (1904); G. K. Rollefson and C. F. Oldershaw, *J. Am. Chem. Soc.*, **54**, 977 (1932).
9) R. Tsuchida and M. Kobayashi, "The Color and the Structure of Metallic Compounds", Zoshindo, Osaka (1944), p. 180 (in Japanese).

in Fig. 1. It has been found by the present measurements that for the band at 52×10^{13}/sec. the A-absorption in Fig. 1 is at least ten times stronger than the B-absorption. The difference in intensity between the two absorptions was so great that exact determination of the dichroic ratio could not be made.

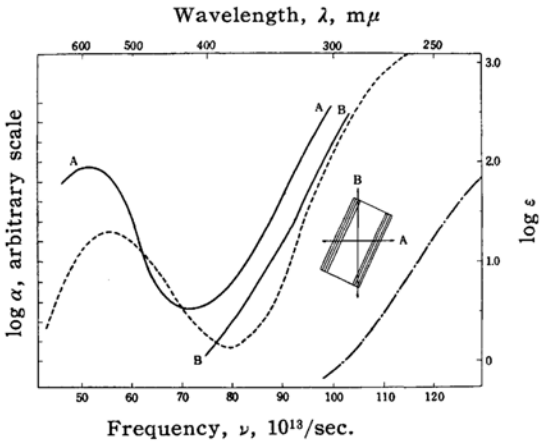


Fig. 1. Absorption spectra of a mixed crystal from $K_2(O_3S)_2$ NO and $K_2(O_3S)_2$·NOH, and its components: the mixed crystal in the solid state, ——: $K_2(O_3S)_2$·NO in 5% KOH solution, – – –: $K_2(O_3S)_2$·NOH in water, ·—·—.

Comparison of the absorption spectrum of the mixed crystal with the spectra of $K_2(O_3S)_2NOH$ and $K_2(O_3S)_2NO$ in solution (Fig. 1) reveals that the band at 52×10^{13}/sec. of the mixed crystal in the solid state may evidently be ascribed to the component, $K_2(O_3S)_2NO$, since the other component has no absorption in the neighborhood of this absorption band. It is presumed, in a similar way, that the state of the peroxylamine disulfonate ion in the mixed crystal is similar to that of Fremy's salt in water. Previously Asmussen[7] concluded from magnetic measurements that $K_2(O_3S)_2NO$ in aqueous solution consists largely of monomeric ions; the three-electron bond is usually assumed to be involved in the bonding within the NO-group of the monomer. Therefore, it may be certain that Fremy's salt exists as a monomeric form when incorporated into the mixed crystal with $K_2(O_3S)_2NOH$. Thus the band at 52×10^{13}/sec. of the mixed crystal may be ascribed to the $(O_3S)_2NO^{2-}$ ions under the effect of the field by the surrounding ions. The band is, therefore, regarded as due primarily to the NO-group in the monomeric ion under small perturbation from the surrounding ions, although the bonding around the NO-group should not be considered, in a strict sense, to be isolated from the other part of the ion. The present measurements show that *the NO-band, in which the three-electron bond may be involved, is highly polarized.*

The effects of solvents upon the absorption band have also been examined. Formerly the "nitroso-band" at about 700 mμ of nitroso-derivatives and the band at about 350 mμ of a nitrite ion were reported to undergo a "blue solvent effect"[10]. This fact was then assumed to show that both the bands were due to $n-\pi^*$ transitions. On the contrary, the present measurements indicate that the absorption band at about 55×10^{13}/sec. (540 mμ) of the $ON(SO_3)_2^{2-}$ ion is displaced to longer wavelengths on changing a solvent from ethanol to water. The "red shift" of the band seems to show that the band may originate from a $\pi-\pi^*$ transition[10], although the intensity of the band is rather small for this type of transition. This appears to be consistent with the electronic structure of the NO group having a sort of three-electron bond, since the absorption band in question may originate from a transition of one of the three bonding electrons to an excited level.

It was reported earlier that the above mentioned bands, ascribed to the $n-\pi^*$ transition, were polarized perpendicularly to the plane of the NO-group in nitrosobenzene and its derivatives[11] or to the plane of an NO_2^- ion[12]. As for the band of the monomeric ion of $ON(SO_3)_2^{2-}$, which possibly originates from a $\pi-\pi^*$ transition and may be different in its origin from the above mentioned bands, we are inclined to regard it likely that the polarization of the band would be along the plane of the NO-group. Thus the A-absorption in Fig. 1 may correspond to the electric vector along the NO-group, and the B-absorption to the electric vector perpendicular to the NO-group. In order to confirm this suggestion, however, further study seems to be desirable.

Infrared Absorption Spectra. — Results of the present measurements are shown in Table I. Tentative assignment of the

10) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952); M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950), etc.
11) K. Nakamoto and K. Suzuki, *J. Chem. Phys.*, **20**, 1971 (1952).
12) W. G. Trawick and W. H. Eberhardt, ibid., **22**, 1462 (1954); J. W. Sidman, *J. Am. Chem. Soc.*, **78**, 2911 (1956).

TABLE I. INFRARED ABSORPTION SPECTRA OF FREMY'S SALT AND RELATED COMPOUNDS IN THE SOLID STATE

Tent. Assign.	Mixed crystal $K_2(O_3S)_2NOH+K_2(O_3S)_2NO$*		$K_2(O_3S)_2NOH$		(presumed) $K_2(O_3S)_2NO$		$K_4[(O_3S)_2NO]_2$	
O-N-SO_3	870	m	870	m	860~870	m	850	m
H-O-N	980	m	945	m				
SO_3	1030	s	1030	s				
SO_3	1050	s			1050	s	1050	s
SO_3	1085	m	1070	m	1080	m	1070	s
SO_3	1260	s	1255	s				
SO_3	1285	s			1285	s	1290	s
NO-str.	1620	m			1620	s	1260	s

* A very small amount as compared with the other component.

s: strong, m: medium intensity.

observed absorption bands to particular group-vibrations was made using the assignment by Drago[13] for $K_2(O_3S)(NO)_2$ and by Griffith and others[14] for Fremy's salt. Griffith and others have also reported the infrared absorption spectrum with Fremy's salt[15]. Unfortunately they did not state whether the measurements refer to the compound in the solid state, or in aqueous solution. Their measurements were probably made in the solid state in which the compound consists of the dimeric form, since their data agree with ours for the $[(O_3S)_2NO^{2-}]_2$ ion. They have not presented any detailed discussion about the infrared spectrum or the structure of the dimer, but mentioned the compound as having an N–N linkage. It seems, however, that no reports have appeared which may be regarded to establish the structure of the dimeric ion with certainty, as far as literatures accessible to us are concerned.

The infrared absorption bands of the monomeric $ON(SO_3)_2^{2-}$ ion were determined by comparing an absorption spectrum of the mixed crystal from Fremy's salt and potassium hydroxylamine disulfonate with the spectrum of the latter alone. Although some effects, such as hydrogen bonds, which possibly exist in the mixed crystal, are liable to complicate the spectrum and make the exact assignment of the absorption bands difficult, the interpretation of the absorption spectrum of $K_2(O_3S)_2NO$ has been possible. In a strict sense, the infrared absorption bands are not to be ascribed to particular groups within a molecule, but to a molecule or an ion as a whole. Nevertheless, the discussion, as is given here, may be correct for the nature and the purpose of the present work.

The vibrations which are ascribed to the $(O_3S)_2NO^{2-}$ ion in the mixed crystal are given in Table I, where the vibrations due to the sulfonate groups are added together, since the ion would certainly show the vibrations of the sulfonate groups. A rather strong band at 1620 cm^{-1} of the monomeric $(O_3S)_2NO^{2-}$ ion may be due possibly to an NO-stretching vibration. This assignment is regarded as reasonable, in view of the NO-frequencies which were formerly reported for other compounds: nitroalkyls[16] 1560~1500 and 1350~1300 cm^{-1}, dimeric nitrosomethane[17] 1282 cm^{-1}, nitrosamine 1455 cm^{-1} in a monomeric form and 1310 cm^{-} in a dimeric form[18]. Thus the rather high frequency of the NO-vibration for the monomeric $(O_3S)_2$ NO^{2-} ion is found to correspond to comparatively high bond-order of the NO-linkage, being in agreement with the assumption of the three-electron bond.

The Structure of the Dimeric Form of Fremy's Salt. — The structure of the dimeric form of Fremy's salt has formerly been examined by a number of investigators. Hantzsch and Semple[5] assumed that the violet-blue and the yellow form are, respectively, the monomeric and the dimeric form of Fremy's salt, comparing the relation between them to that between nitrogen dioxide and dinitrogen tetroxide. Investigating chemical property of Fremy's salt in aqueous solution, Haga and Divers[6] proposed a structure, $K_4(O_3S)_2NO\cdot ON(SO_3)_2$, for the monomeric form of Fremy's

13) R. S. Drago, ibid., **79**, 2049 (1957).

14) W. P. Griffith, J. Lewis and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 38 (1958).

15) They denote Fremy's salt as $K(O_3S)(NO)_2$, but the compound should be represented by an empirical formula of $K_2(O_3S)_2NO$, as has usually been adopted for the compound.

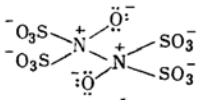
16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen and Co., London (1954).

17) B. G. Gowenlock and J. Trotman, *J. Chem. Soc.*, **1955**, 4190.

18) R. n. Haszeldine and B. J. H. Mattinson, ibid., **1955**, 4172.

salt in solution and double the formula for the dimeric form. Much later, Asmussen[7] investigated the compound magnetochemically only to reaffirm Hantzsch and Semple's hypothesis, and regarded that Fremy's salt in aqueous solution exists as an equilibrium mixture consisting of a monomeric form in most part and a dimeric form in a very small amount. Neither Asmussen nor Hantzsch and Semple, however, presented a structural formula for the dimer after all. The structures, as proposed long ago for the dimer of Fremy's salt by Rasching[3] and by Claus[4], are not quite satisfactory, in view of insufficient materials available as well as because of poor knowledge at that time about the chemical bonds in general. Thus the problem of the structure of the dimer is not to be regarded as settled, but reexamination of the structure seems to be most desirable.

Examination of the possible electronic structures seems to indicate that the following three configurations (Fig. 2) may most probable for the dimer, the structures with resonance which involves the sulphonate-groups being omitted.



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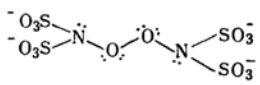

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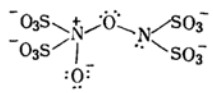

III

Fig. 2. Possible configurations for the dimeric form of Fremy's salt.

Examination of the steric requirements using molecular models shows that structure I seems to be very difficult, although it might not be quite impossible. Thus crowding of one oxygen atom and two sulfonate-groups around the nitrogen atom would hinder dimerization through an N–N linkage. Structure III is also difficult sterically, although this may not be impossible. On the other hand, structure II suffers no steric hindrance. Structure II, therefore, seems to be most probable from this standpoint.

The present measurements of UV spectra show that the electronic state of the dimer deviates greatly from the state of the monomer, since the UV absorption spectrum of Fremy's salt in the crystalline state is quite different from that of the monomer (Fig. 3). Thus the absorption band at about 55×10^{13}/sec., which is due primarily to the NO-group in the monomer, disappears with the dimer. Instead, the latter shows a few absorption

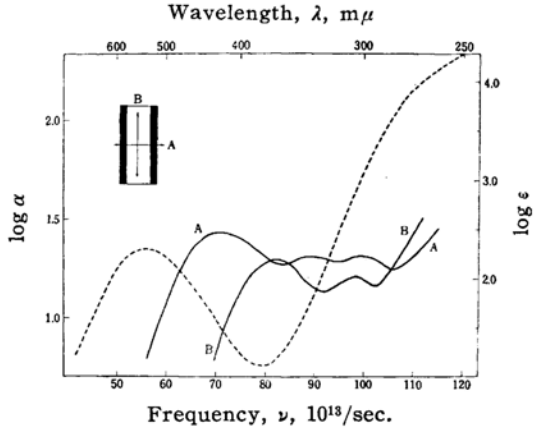

Fig. 3. Absorption spectra of Fremy's salt in the crystalline state (——) and in aqueous solution (----).

bands in the visible region and its neighborhood. If the dimer were represented by structure I, it would not exhibit an absorption band in the visible region, as is readily expected from absorption spectra of its related compounds. Previous data indicate that the dimer of nitrosomethane, which has a configuration similar to structure I, shows an absorption band at about 280 mμ (107×10^{13}/sec.) but no absorption band in the visible region, much less the "nitroso-band" at about 650 mμ (46×10^{13}/sec.). Since inspection of the structural formulae shows that structure I might involve N–O bonds with lower bond order than that of the N–O bond in the dimer of nitrosomethane, the ion represented by structure I would not show an absorption band in the neighborhood of the visible region. In fact, the present measurements indicate that the dimer of Fremy's salt has a few absorption bands in this wavelength range. Structure I, therefore, is rejected on the basis of the UV absorption spectra as well as of the steric requirements.

Absorption spectra of the compounds

which are somewhat similar to the compound represented by structure II have previously been studied. Thus Kortüm and Finckh[19] reported absorption spectra of sodium nitrite, pernitrite, hyponitrite and related compounds in solution, which were found to display absorption bands in the comparatively long wavelength region. Structure II, therefore, may not be inconsistent with the present observation that the compound in question displays absorption bands in the visible region and its neighborhood. Structure III, however, may not be excluded from the visible and ultra-violet spectrum alone.

The above discussion on the structure of the dimer of Fremy's salt is corroborated by the infrared absorption spectra. It is seen in Table I that the monomeric ion of $(O_3S)_2NO^{2-}$ shows a strong band at about 1620 cm^{-1} which is due to the N–O stretching vibration, whereas the dimeric ion shows the corresponding bands at 1260 cm^{-1}. Structure III would show the corresponding bands of high intensity due to the N–O stretching vibrations at wavenumbers smaller than the vibration of the monomer. Thus, at least a few absorption bands due to the N–O stretching vibrations might be observed in the infrared spectrum for structure III, since three kinds of the NO-groups are involved in this structure and those vibrations are all infrared active. The fact that there is observed only one absorption band of this sort for the dimer is not consistent with structure III, although a possibility might remain that some of the absorption bands would be hidden under strong bands due to the sulfonate groups.

On the contrary, structure II has only one kind of N–O bond, and the symmetric vibration due to the NO groups is infrared inactive. Only the symmetric vibration is infrared active, and may be regarded as corresponding to the band at 1260 cm^{-1}. Thus the infrared spectrum may be reconciled in a satisfactory way with structure II. Further evidence for this conclusion may be obtained by complete analysis of the infrared absorption spectra, which, however, requires data of the Raman spectrum with this compound. The determination of it would be enlightening in this respect. Based on the infrared spectrum alone, structure I might also be possible, but this structure has been shown in the preceding part of the present paper to be inconsistent with the UV spectra and steric requirements.

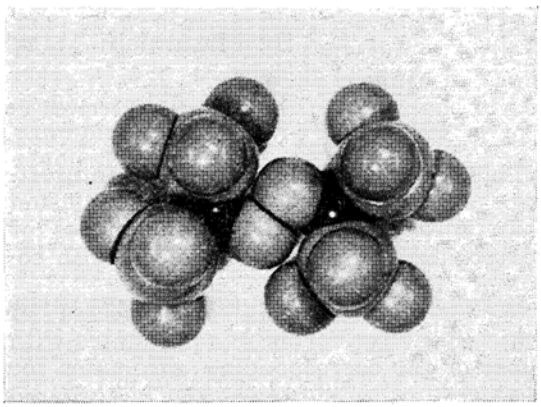

Fig. 4. Stuart model of $(O_3S)_2NO \cdot ON(SO_3)_2^{4-}$.

All the above materials combined seem to favour most strongly structure II having an O–O linkage. — A Stuart model representing structure II is shown in Fig. 4. This conclusion on the structure of the dimer seems to be noteworthy, since it is known that most nitroso-derivatives tend to form dimers involving a linkage of an N–N type.

Summary

Absorption spectra in the visible and ultra-violet region have been determined at room temperature by Tsuchida and Kobayashi's microscopic method with crystals of Fremy's salt and related compounds. Infrared absorption spectra have also been measured with these compounds.

The results of the measurements are discussed in relation to the structure of the compounds. A steric condition, visible and ultra-violet absorption spectra and infrared spectra are found to be in best agreement with a structure having a peroxide grouping.

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19) G. Kortüm and B. Finckh, *Z. physik. Chem.*, **B48**, 32 (1941).