

not so large, with $dtpa$. Such unusual spectrochemical behavior clearly parallels the unusual features of chemical reactivity, *i.e.*, easy oxidizability, of $Nidtb_2$. At present, our experimental data do not indicate any simple, obvious interpretation of this behavior; it is probably to be related to the extension of π conjugation in dtb over a larger framework, including both the $-CSS-$ group and the phenyl ring (actually, Bonamico's work

shows that the C-C distance between C_6H_5 and CS_2^- is short enough to suggest conjugation between the two groups), and possibly also to intraligand conjugation effects occurring between both L units in a square-planar complex, *i.e.*, to the same cause leading to the well-known peculiar chemical and spectrochemical properties of complexes containing stable square-planar matrices.²⁰

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An Investigation of Crystalline Paramagnetic Salts of Nitrosyldisulfonate Ion

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Received March 28, 1968

The preparation and determination of several salts of the free radical nitrosyldisulfonate ion are reported. These all have one unpaired electron per anion, as indicated by magnetic susceptibility measurements. The pure salts gave broad epr signals, but after dilution with a diamagnetic solid, or after partial decomposition, hyperfine splittings appeared.

The violet free radical nitrosyldisulfonate ion, $ON(SO_3)_2^{2-}$, has been the subject of numerous kinetic and electron paramagnetic resonance studies. The most common solid salt of this ion is that of potassium (Fremy's salt). This salt is diamagnetic, is golden yellow, and is believed to contain the dimeric ion.

The most commonly used form of this ion is that of the potassium salt in aqueous solution, made alkaline to enhance the stability. The salts of tetraphenylarsonium and tetraphenylstibonium cations have been used in nonaqueous solutions in certain epr studies^{2,3} and the solid tetraphenylstibonium salt was reported used in one study as a polycrystalline mass.⁴ No preparation, analysis, or purity information was reported. The free-radical ion has also been studied in solid potassium hydroxylamine disulfonate.⁵

We have succeeded in preparing a number of salts of this ion using cations larger than potassium. They are violet and are paramagnetic, with about one unpaired electron per anion. Epr properties of these salts are reported, along with the effects noted as the concentration of the free radical is changed.

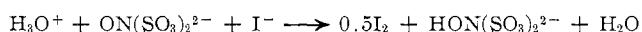
Experimental Section

Preparation of Cesium Nitrosyldisulfonate.—A solution of the sodium salt was prepared by the method of Murib and Ritter.⁶ This solution was saturated at room temperature with solid cesium chloride, after which it was filtered and cooled to 0°. The violet-blue needle-like crystals which formed were filtered off and recrystallized from 0.35 *N* cesium hydroxide at 50°. The crystals were washed with a small amount of cold water and

then with absolute methanol, dried, and stored in a vacuum desiccator. These crystals gave no precipitate with a silver nitrate solution.

The salt was soluble in water, but insoluble in alcohol, acetone, nitromethane, and benzene. It is quite unstable and could be preserved in a vacuum desiccator for only a few hours.

This salt was analyzed by iodimetry. A few crystals of solid potassium iodide were added to an aqueous solution of the salt which was then acidified. The iodine produced by the reaction



gave the oxidizing equivalent weight 454; the calculated weight was 456. This purity (99.6%) was confirmed by determination of cesium by flame photometry and analysis of the colored anion by optical density measurements, using a Beckman DU spectrophotometer and the molar extinction coefficient of 20.8 at 545 $m\mu$.⁶

Preparation of Tetraphenylarsonium Nitrosyldisulfonate.—Solid potassium nitrosyldisulfonate was added to a saturated aqueous solution of tetraphenylarsonium bromide, prepared by the method of Chatt and Mann.⁷ The product precipitated on vigorous stirring. The suspension was cooled in ice water and filtered. The salt was washed with much cold water and then with anhydrous ether, dried, and stored in a vacuum desiccator. These crystals were quite insoluble in water and benzene but dissolved in chloroform, acetone, and similar solvents. Attempts at recrystallization resulted in considerable loss of product with no increase in purity, so in most preparations no recrystallization was attempted. This salt was quite stable if protected from moist air. A sample in an evacuated tube showed no change in magnetic susceptibility for well over 1 month.

Iodimetric determination was unsuited for this salt as the cation precipitates with triiodide ion. This suggested the alternate method of adding triiodide solution to a weighed sample to precipitate tetraphenylarsonium triiodide, which was collected on a filter, washed with water, dried at 100°, and weighed. This method indicated a purity of at least 99%. The most precise determination involved a potentiometric titration with ferrous

(1) The author to whom inquiries should be addressed.

(2) J. Townsend, S. I. Weissman, and G. E. Pake, *Phys. Rev.*, **89**, 606 (1953).

(3) B. Smaller and E. Yasaitis, *J. Chem. Phys.*, **21**, 1905 (1953).

(4) T. L. Chu, G. E. Pake, D. E. Paul, J. Townsend, and S. I. Weissman, *J. Phys. Chem.*, **57**, 504 (1953).

(5) S. I. Weissman and D. Banfill, *J. Am. Chem. Soc.*, **75**, 2534 (1953).

(6) J. H. Murib and D. M. Ritter, *ibid.*, **74**, 3394 (1952).

(7) J. Chatt and F. G. Mann, *J. Chem. Soc.*, 1192 (1940).

ion. This yielded a purity of 99.6% for the recrystallized product.

Preparation of Tetraphenylstibonium Nitrosyldisulfonate.—This salt was prepared as was the previous salt. It was insoluble in water, carbon tetrachloride, ether, and *n*-hexane but was readily soluble in alcohol, chloroform, acetone, and nitromethane. It was readily recrystallized from a 10% acetone–water solution.

Determination by barium sulfate precipitation after decomposition of the salt indicated a purity of 99.9%. Potentiometric titration with ferrous ion indicated a purity of 99.5%. For a colorimetric determination a sample of the salt was placed in 1 *M* potassium hydroxide and stirred vigorously. The insoluble tetraphenylstibonium hydroxide which formed was removed and the violet filtrate and washings were diluted to volume in a volumetric flask and analyzed colorimetrically as was the cesium salt.

Preparation of Tetramethylammonium Nitrosyldisulfonate.—An ion-exchange column was prepared using 20 ml of Dowex 50W. Through this was passed a 10% solution of tetramethylammonium hydroxide, followed by water. A solution of 1.2 g of potassium nitrosyldisulfonate in 60 ml of very dilute NaOH solution (pH 11) was passed through the column, followed by water. The first 13 ml of eluate was discarded. The following 50 ml of eluate was collected and placed in a rotary evaporator with a few drops of tetramethylammonium hydroxide to preserve the product. On evaporation almost to dryness, nice violet crystals formed. These were removed and blotted dry.

These crystals were insoluble in hot ethanol, carbon tetrachloride, and chloroform but readily soluble in water. An iodimetric determination revealed a purity of about 98%. Traces of potassium and some tetramethylammonium hydroxide to preserve them were present. A moist mass of these crystals remained unchanged for over 1 year.

Attempted Preparation of the Hexaamminecobalt(III) Salt.—Solid potassium nitrosyldisulfonate was added to a saturated solution of hexaamminecobalt(III) chloride. The brown precipitate was collected on a filter and washed with cold water and methanol. This product was found to be soluble only in hot water. Ferrous ion potentiometric titrations indicated a purity of about 70%, while magnetic susceptibility measurements indicated $n = 1.6$, suggesting that a product different from $[\text{Co}(\text{NH}_3)_6]_2[\text{ON}(\text{SO}_3)_2]_3$ was obtained. This substance is to be investigated further.

Preparation of Other Salts.—The sodium and ammonium salts were too soluble in water to be prepared easily. The rubidium salt was obtained and had a color intermediate between yellow and violet, suggesting it might be a mixed crystal.

Magnetic Measurements.—A magnetic balance was assembled using an electromagnet with a field strength variable from 4430 to 5500 G. The field was calibrated with $\text{HgCo}(\text{SCN})_4$ with a reported specific susceptibility of 16.44×10^{-6} cgsu.

Epr Measurements.—A Varian 4500-10A epr control unit with a Spectromagnetic Industries Model L 12-A 12-in. magnet was used, along with a Varian V-FR 2100 field-regulated magnet power supply. The frequency of the cavity was measured with a Hewlett-Packard transfer oscillator, Model 540B, and electronic counter, Model 524C. The field was calibrated using crystalline DPPH with a *g* value of 2.0037. The samples were attached as a polycrystalline mass to a Teflon rod and inserted into a Varian multipurpose cavity. Most work was done at about 3400 G and about 9000 Mc/sec.

Results

Magnetic Measurements.—Owing to the very high molecular weights of these salts, their diamagnetism was appreciable and could not be ignored; hence the reported paramagnetism is highly dependent on the calculated diamagnetism, as shown in Table I.

Epr Results.—The spectra for high-purity samples of

TABLE I
MAGNETIC MEASUREMENTS

	H, G	Diamag- netism ^a ×		<i>n</i> ^b
		10 ⁶ χ _M , cgsu	10 ⁶ χ _M ', cgsu	
Cs ⁺ salt Mol wt 455.96	4430	95.1	15.2	110 0.91 ± 0.03
	4900	91.0	15.2	106 0.89
	5500	91.4	15.2	106 0.89
(C ₆ H ₅) ₄ As ⁺ salt Mol wt 956.7	4430	109.0	58	167 1.25 ± 0.05
	4900	97.6	58	156 1.18
	5500	95.2	58	153 1.17
(C ₆ H ₅) ₄ Sb ⁺ salt Mol wt 1051.5	4430	58.3	65	123 0.99 ± 0.05
	4900	48.0	65	113 0.94
	5500	46.5	65	112 0.93
Co(NH ₃) ₆ ³⁺ salt Mol wt 892	4430	185.5	39.6	225 1.55 ± 0.05 ^c
	4900	202	39.6	242 1.61
	5500	200	39.6	240 1.60

^a Calculated from data of J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960. ^b The "spin-only" formula was used: $2.84 \times (\chi_M' T)^{1/2} = \sqrt{n(n+2)}$. ^c Calculated for $[\text{Co}(\text{NH}_3)_6]_2[\text{ON}(\text{SO}_3)_2]_3$.

all these salts, except the tetraphenylarsonium salt, consisted of one broad absorption line. When the sample was allowed to stand for a time so as to decompose partially, or when it was diluted with a diamagnetic solid, the single line split into three symmetrical lines.

TABLE II

EPR RESULTS

	Broad-line width (between points of extreme slope)	Width between splittings,	<i>g</i> value ^a
	G	G	
Cs ⁺ salt	47	12.9	2.0111
(C ₆ H ₅) ₄ As ⁺ salt		13.3	2.0056
(C ₆ H ₅) ₄ Sb ⁺ salt	107	13.6	2.0053
(CH ₃) ₄ N ⁺ salt	35	12.6	2.0056

^a Calculated from the formula $g = 0.7145(\nu/H)$, where ν is in megacycles, and *H* is in gauss.

Attempts were made to align single crystals in the cavity and obtain rotation data. Only the cesium salt produced suitably shaped crystals; they are the least stable, however, and each one decomposed before it could be aligned.

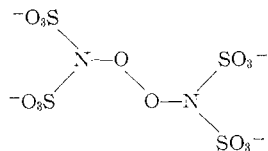
Discussion

These salts are all fairly unstable. Most faded slowly over a period of hours or days; however, the cesium salt often decomposed rapidly leaving a white fused mass. Murib and Ritter⁶ noted a decrease in stability of the ion in the presence of chloride ion, but in this study preparations involving salts other than cesium chloride did not improve the stability of the salt. The alkali metal, ammonium, and tetramethylammonium salts of nitrosyldisulfonate are all readily soluble in water. The tetraphenylarsonium and tetraphenylstibonium salts are soluble only in polar solvents such as nitromethane, acetone, etc. No salts were found soluble in nonpolar solvents such as benzene.

Two effects are noted as the concentration of the

free-radical ion in the solid is varied by using different cations:

(1) **The Monomer-Dimer Effect.**—The potassium salt in solution or in a mixed crystal with potassium hydroxylamine disulfonate exists as a monomer, but in the pure solid it is dimerized. Yamada and Tsuchida⁸ conclude that steric conditions, along with visible, ultraviolet, and infrared spectra, suggest a structure having a peroxide linkage



Nothing is known from X-ray crystal studies about the actual structure of the dimer. As the cation size increases a critical size is reached above which the cation prevents dimerization, probably owing to steric hindrance. As shown in Table III, this size is about that of the rubidium ion. Hoffman and Henderson reported⁹ the preparation of the stable di-*t*-butyl nitroxide free radical, $[(\text{CH}_3)_3\text{C}]_2\text{NO}$. It was suggested that steric hindrance of the two *t*-butyl groups on the nitrogen prevents dimerization.

(2) **Exchange and Hyperfine Splitting Effects.**—With tetraphenylstibonium ion in the pure solid and in a 0.5 M solution only one broad peak was observed.¹⁰

(8) S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **32**, 721 (1959).

(9) A. K. Hoffman and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).

(10) G. Pake, J. Townsend, and S. Weissman, *Phys. Rev.*, **85**, 682 (1952).

TABLE III

Cation	ION SIZE AND MAGNETIC PROPERTIES	
	Radius, Å	Magnetic properties of the salt
Na ⁺	0.97	Diamagnetic
K ⁺	1.33	Diamagnetic
Rb ⁺	1.47	Not measured; its color suggests it is a mixed crystal of both the monomer and the dimer
Cs ⁺	1.67	Paramagnetic
(CH ₃) ₄ N ⁺	~2.4 ^a	Paramagnetic
(C ₆ H ₅) ₄ As ⁺	~6.3 ^a	Paramagnetic
(C ₆ H ₅) ₄ Sb ⁺	~6.5 ^a	Paramagnetic
Co(NH ₃) ₆ ³⁺	~2.8	Paramagnetic

^a Calculated from data of R. C. L. M. Slater, *Acta Cryst.*, **12**, 187 (1959).

This is due to spin-spin interaction of nearby free-radical neighbors. When the concentration of the radicals is lowered the hyperfine splittings appear, as was noted in this study with a sample diluted with a diamagnetic salt or partially decomposed. The broad line split into three equidistant peaks of about 13-G separation, comparable to the splitting observed in very dilute solutions by the nitrogen nuclear spin.

Of interest to clarify the monomer-dimer situation will be X-ray crystal studies, preliminary phases of which are under way in our laboratories, and single-crystal anisotropy epr studies, once the problem of preparing suitable stable crystals is solved.

It should also be possible to correlate the spin-spin interaction effect with the distance of separation of the free radicals, both in solution and in solid salts once this structure information is available.

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Some Tetrazole Complexes of Transition Metal Halides

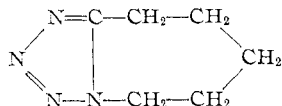
By DELORES M. BOWERS AND ALEXANDER I. POPOV

Received February 8, 1968

Anhydrous complexes of pentamethylenetetrazole (PMT) were prepared with first-row transition metal chlorides and bromides. Two types of complexes were isolated, $\text{M}^{\text{II}}(\text{PMT})\text{X}_2$ and $\text{M}^{\text{II}}(\text{PMT})_2\text{X}_2$. Both types of compounds are quite insoluble in polar and nonpolar liquids and have high melting or decomposition points. Magnetic and spectral evidence indicate that the metal ions in the $\text{M}^{\text{II}}(\text{PMT})\text{X}_2$ complexes are in octahedral environments while $\text{M}^{\text{II}}(\text{PMT})_2\text{X}_2$ complexes may be tetrahedral. The former compounds are probably polymeric and contain halogen bridges, while complexes containing two molecules of the ligand are probably monomeric and have tetrahedral structure.

Introduction

In previous communication from this laboratory^{1,2} we reported the preparation and some properties of complexes formed by pentamethylenetetrazole (PMT) with some first-row transition metal perchlorates.



(1) H. A. Kuska, F. M. D'Itri, and A. I. Popov, *Inorg. Chem.*, **5**, 1272 (1966).

(2) F. M. D'Itri and A. I. Popov, *ibid.*, **5**, 1670 (1966); **6**, 597, 1591 (1967).

These complexes had the general formula $\text{M}^{\text{II}}(\text{PMT})_6(\text{ClO}_4)_2$ with M^{II} being Fe, Mn, Co, Ni, Zn, or Cu. It was shown that the complexes had octahedral or a distorted octahedral configuration. They were soluble in water and in a number of polar nonaqueous solvents. Magnetic susceptibility measurements have indicated that the complexes were of high-spin type.

Initial studies were carried out with perchlorates since we desired to minimize the possibility of interference from the anion and the formation of mixed complexes. The ligand, however, does not seem to have very strong donor properties and more polarizable