

methyl iodide in benzene and successive treatment with aqueous KClO_4 solution gave colorless crystals of 1,2-bis(diisopropylamino)-3-methylthiocyclopropenium perchlorate (**5a**, $R_1 = R_2 = i\text{-Pr}$, $R_3 = \text{Me}$) quantitatively, mp 157° . The prominent ir bands of **5a** appear at 1899 and 1547 cm^{-1} ; uv (MeOH) λ_{max} 266 nm ($\log \epsilon$ 3.91), 214 (4.02); nmr (CDCl_3) τ 8.62 (doublet, 24 H), 7.24 (singlet, 3 H), 6.02 (sextet, 4 H). Di-*tert*-butylmethylaminocyclopropenone (**2b**) and the corresponding thione (**3b**) were obtained by similar procedures in moderate yield.

It has been reported that tetramethylurea forms a stable acid adduct formulated as $((\text{CH}_3)_4\text{N}_2\text{CO})_2 \cdot \text{HSbCl}_6$.^{6b} One can point out a striking similarity of **2** to tetraalkylurea in the chemical behavior. The reaction of **3a** with methyl iodide (electrophile) is also similar to the corresponding reaction of thioureas. These chemical properties are explainable if we assume that the three-membered ring corresponds to a sp^2 carbon atom. In this sense, we can call diaminocyclopropenones and diaminocyclopropenethiones quasi-urea and quasi-thiourea, respectively.

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Matrix Raman Spectrum of the Fluorine Molecular Anion, F_2^-

Sir:

As early as 1955, Känzig¹ postulated the existence of F_2^- as observed in the electron spin resonance spectrum of γ -irradiated crystalline LiF at 77°K . In later work, Delbecq, *et al.*,² reproduced the Känzig results on F_2^- while Vande Kieft and Gilliam³ produced the F_2^- species by irradiating alkali bifluoride salts M^+HF_2^- . Balint-Kurti and Karplus⁴ have performed potential energy surface calculations for the reaction $\text{Li} + \text{F}_2 \rightarrow \text{LiF} + \text{F}$. Even though this reaction is exothermic by approximately 100 kcal/mol, there is a stable complex intermediate, isosceles triangular Li^+F_2^- , which has a maximum calculated well depth of approximately 40 kcal/mol.

In view of the potentially limited stability of the M^+F_2^- species, argon matrix reactions of alkali metal atoms and fluorine molecules were used to produce and isolate this reaction product. Fluorine samples in argon

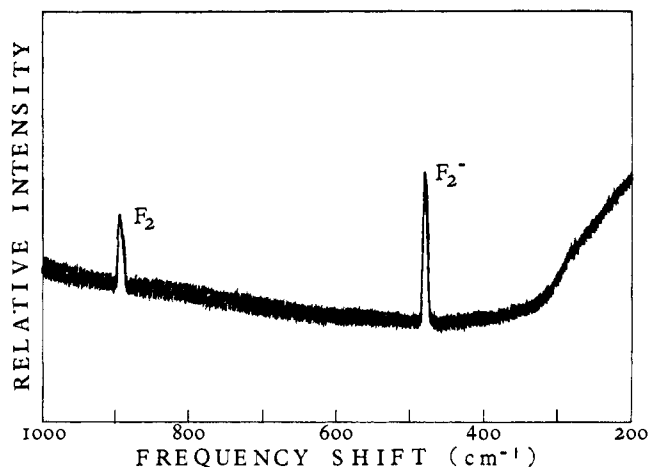


Figure 1. Raman matrix spectrum of fluorine ($\text{Ar}/\text{F}_2 = 50$) reacting with sodium atoms. Instrumental parameters: exciting line approximately 100 mW of 4880 \AA ; range, $0.3 \times 10^{-9}\text{ \AA}$; filter, 5-\AA dielectric spike; rise time, 3 sec; scan speed, $10\text{ cm}^{-1}/\text{min}$.

($\text{Ar}/\text{F}_2 = 50$ and 100) were deposited on a tilted copper wedge maintained near 15°K . An atomic beam of alkali metal was codeposited with the fluorine sample using metal vapor pressures near $1\text{ }\mu$. The experimental technique and spectroscopic and cryogenic equipment have been described previously.^{5,6} Raman spectra from 50 to 1100 cm^{-1} were recorded using approximately 100 mW of 4880 and 5145 \AA excitation from the argon plasma laser. Band positions were determined by calibration with argon fluorescence lines which were superimposed on the spectra during the running scan.

The Raman spectra of alkali metal atom- F_2 matrix reaction products showed only two bands, one at $892 \pm 1\text{ cm}^{-1}$ due to F_2 in excellent agreement with the gas-phase value⁷ and the other near 460 cm^{-1} depending on the particular alkali metal reagent. No metal fluorides (M^+F^-) were observed in the Raman spectrum owing to the very low Raman intensities of such ionic species. Argon matrix frequencies⁸ of LiF, NaF, and KF are accurately known; these spectral regions were void of signal.

Figure 1 shows the spectrum of the sodium- F_2 reaction products. Here the new band appeared at $475 \pm 1\text{ cm}^{-1}$. This feature exhibited instability due to laser photolysis; 10 min of laser illumination decreased the band intensity by approximately one-half. Furthermore, the intensity ratio of the 892 cm^{-1} feature to the 475-cm^{-1} band increased during laser illumination as the lower feature was photodecomposed faster by the laser than F_2 itself. In lithium experiments, the new feature was observed at $452 \pm 1\text{ cm}^{-1}$, 464 ± 1 for K, 462 ± 1 for Rb, and at $459 \pm 1\text{ cm}^{-1}$ for Cs. Clearly, the alkali metal is associated with the new species producing the Raman signal near 460 cm^{-1} .

Due to the photolytic instability of the new product species, depolarization ratio measurements were difficult to make. However, in the sodium case the 475-cm^{-1} band had sufficient intensity to record depolarization data; an average ratio of 0.7 was obtained for the 475-cm^{-1} band. The same depolarization ratio

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was measured for F_2 in these experiments, suggesting that these are similar vibrational modes of similar species. Of course, this depolarization ratio is too high for the Raman fundamental of F_2 and, likewise, it is probably higher than the true value for the 475-cm^{-1} scatterer. Apparently incomplete randomization of molecular orientations and scrambling of the polarized scattered light by the frosty matrix sample cause measured depolarization ratios to be too high in these experiments. The symmetric mode Raman bands for argon matrix isolated⁶ OF_2 produced depolarization ratios which were much higher than those measured from the liquid spectrum.⁹

In order to provide a fluorine analysis of the new species at 475 cm^{-1} , similar reactions were done with sodium and Cl_2 in argon and a Cl_2 - F_2 mixture in argon. With the chlorine-sodium reaction, an intense new band was observed at 225 cm^{-1} which is attributed to the chlorine counterpart, $M^+Cl_2^-$, of the 475-cm^{-1} fluorine band. The Cl_2 - F_2 reaction with sodium showed only two new spectral features, the 475- and 225-cm^{-1} bands. Hence, the new species incorporates one halogen molecule or two halogen atoms and is most probably $M^+F_2^-$. The lack of intermediate spectral features between 475 and 225 cm^{-1} rules out a species containing three halogen atoms.

The Raman bands near 460 cm^{-1} reported here are assigned to the intraionic $(F-F)^-$ stretching mode in the $M^+F_2^-$ species. The interionic $M^+-F_2^-$ mode is being sought in the infrared. The frequency position of this mode influences the Raman frequency of the intraionic $(F-F)^-$ mode. If we may approximate the $M^+-F_2^-$ mode frequency with the analogous $M^+-O_2^-$ modes, the frequencies 699 , 391 , 307 , 255 , and 236 cm^{-1} have been reported for Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ superoxides,¹⁰⁻¹² respectively. The significant point is that there is a frequency cross-over with the interionic and intraionic modes; for $Li^+F_2^-$ the interionic mode appears *above* the intraionic mode forcing it down (452 cm^{-1}) by interaction of vibrational modes of the same symmetry; for $Na^+F_2^-$ the interionic appears *below* the intraionic mode forcing it up (475 cm^{-1}). As the M^+ becomes heavier, the interionic mode rapidly drops diminishing the interaction and the intraionic mode frequency decreases (from 464 to 459 cm^{-1} for K^+ to Cs^+).

The additional electron in F_2^- is added to an antibonding σ molecular orbital thus reducing the number of net bonding electrons from two for F_2 to one for F_2^- . A casual approximation of the F_2^- vibrational frequency would be half that of F_2 . It is gratifying that the F_2^- frequency falls near 50% of the F_2 fundamental. The $M^+F_2^-$ species observed here is, in many ways, analogous to the $M^+O_2^-$ species observed in alkali metal atom- O_2 matrix reactions.¹⁰⁻¹³ In the superoxide species, oxygen isotopic mixtures showed the two oxygen atoms to be equivalent in an isosceles triangular structure and the $O-O$ stretching modes corresponded to $(O-O)^-$ vibrations.

The evidence presented here strongly justifies the

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production and stabilization of F_2^- as the species $M^+F_2^-$ from the matrix reactions of alkali metal atoms and molecular fluorine. The ion-molecule is unstable as expected and it shows a bond similarity to F_2 from polarization data. The comparative vibrational frequencies of F_2 and F_2^- correspond to a rough molecular orbital prediction. Lastly, the frequency dependence upon the alkali metal reagent is not enough for a $M-F$ vibration; it corresponds to a $(F-F)^-$ vibration slightly perturbed by its adjoining alkali cation partner.

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Triple-Decked Sandwich Compounds. Planar $C_2B_3H_5^{4-}$ Cyclocarborane Ligands Analogous to $C_3H_5^-$

Sir:

The metallocarboranes, or metal-carborane π complexes,¹ are conveniently regarded as electronic analogs of the metallocenes, and a formal 6-electron donation from each carborane ligand (considered as a dianion) to the metal atom is normally assumed. With the following exception, all previously reported metallocarborane ligands are three-dimensional boron-carbon cages rather than planar ring systems. Recently, we prepared a diamagnetic $(\pi-C_2B_3H_7)Fe(CO)_3$ complex^{2,3} and from spectroscopic data proposed a structure, subsequently confirmed by an X-ray study,⁴ in which the formal $c-C_2B_3H_7^{2-}$ ligand (isoelectronic with $C_3H_5^-$) is planar except for two B-H-B bridging hydrogens which are directed away from the metal atom. This compound is thus a structural and electronic analog of the well known $(\pi-C_3H_5)Fe(CO)_3^+$ ion. The $C_2B_3H_7^{2-}$ ligand, which has not been prepared as a free anion, may be regarded as a bridge-diprotonated derivative of the cyclic planar $C_2B_3H_5^{4-}$ system, previously unknown. We describe here the first complexes containing the formal $C_2B_3H_5^{4-}$ ligand, which are also the first definitively characterized triple-decked sandwich species having three planar ring systems (Figure 1). These compounds have been characterized from their ¹¹B and ¹H nmr spectra, unit- and high-resolution mass spectra, infrared spectra, and an X-ray diffraction study of III. The close chemical and spectral similarity between III and the other compounds leaves no doubt as to the gross triple-decked structures of all three species. All of the compounds are diamagnetic air-stable crystalline solids in which the formal oxidation state of cobalt is conveniently assigned as +3.

Complex I was obtained from the reaction of 1,6-

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