Soc., **92**, 5114 (1970); R. Mason and G. Rucci, *J. Chem. Soc., Chem. Commun.*, 1132 (1971); M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Dalton Trans.*, 2433 (1973). The CO derivative of hemocyanin has ν_{CO} 2040–2060 cm^{-1}: L. Y. Fager and J. O. Alben, *Biochemistry*, **11**, 4786 (1972); J. O. Alben, L. Yen, and N. J. Farrier, *J. Am. Chem. Soc.*, **92**, 4475 (1970); H. A. Kuiper, R. Torensma, and E. F. J. Van Bruggen, *Eur. J. Biochem.*, **68**, 425 (1976). Small synthetic Cu(I) model compounds which mimic the reversible dioxygen carrying capacity of hemocyanin are known. See ref 6; M. G. Simmons and L. J. Wilson, *J. Chem. Soc., Chem. Commun.*, 634 (1978); C. S. Arcus, J. L. Wilkinson, C. Mealli, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 7564 (1974); M. Pasquali, C. Floriani, and A. Gaetani Manfredotti, *J. Chem. Soc., Chem. Commun.*, 921 (1978).

(9) The reaction of $|2\mathrm{Cu^{II}} \subset \mathbf{1a}|(\mathrm{BF_4})_4$ with superoxide O_2^- slowly yielded a colorless compound. Microcrystalline materials were obtained after reaction with SCN^-, OCN^-, CN^-, $C_2O_4^{2-}$, pyrazine, pyridazine, piperazine, pyrazole, and imidazole. Physical measurements and X-ray studies of the imidazole complex are at present underway.

(10) $|\mathrm{Cu_2(N_3)_4} \subset \mathbf{1a}|$ crystallizes in the monoclinic space group $C2/m$ with a = 10.126 (2), b = 13.246 (3), c = 11.156 (2) Å; β = 93.474 (8)°; Z = 2 formula units per cell. A total of 1084 independent nonzero reflections were measured on a Philips PW 1100 diffractometer and 954 reflections with $I > 3\sigma(I)$ were used in subsequent structure solution and least-squares refinement. Final refinements with anisotropic thermal parameters for all nonhydrogen atoms converged to $R_F = 0.038$ and $R_{wf} = 0.051$.

(11) For structurally characterized Cu(II) azide complexes having the $Cu_2(N_3)_2$ ring, see T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, **17**, 444 (1978) ($|\mathrm{Cu_2(Me_5dien)_2(N_3)_3}|(\mathrm{BPh_4})_2$); the data for this complex are d_{Cu-Cu} = 5.227 (7) Å and $J = -6.5$ cm^{-1}. This $M_2(N_3)_2$ ring is recognized in few complexes with M = Cu(I), Ni(II): $\mathrm{Cu_2^I(PPh_3)_4(N_3)_2}$, R. F. Ziolo, A. P. Gaugnan, Z. Dori, C. G. Pierpont, and R. Eisenberg, *Inorg. Chem.*, **10**, 1289 (1971); $|\mathrm{Ni_2(tren)_2(N_3)_2}|(\mathrm{BPh_4})_2$, C. G. Pierpont, D. N. Hendrickson, D. M. Duggan, F. Wagner, and E. K. Barefield, *Inorg. Chem.*, **14**, 604 (1975).

(12) For comparison with structures of azide complexes, see ref 11; R. F. Ziolo, M. Allen, D. D. Titus, H. B. Gray, and Z. Dori, *Inorg. Chem.*, **11**, 3044 (1972); U. Müller, *Struct. Bonding (Berlin)*, **14**, 141 (1973).

(13) Variable-temperature susceptibility measurements were recorded on a Foex–Forrer translation balance between 390 and 100 K and on a Foner magnetometer in the range of 4–120 K. $\mathrm{HgCo(SCN)_4}$ and platinium metal were used for calibration. Diamagnetic corrections χ_D were applied for all nonmetallic atoms using tabulated values of Pascal's constants: $\chi_D = -333\ 10^{-6}$ cgs mol^{-1}.

(14) Complete diamagnetism of nonbiological dicopper(II) compounds has been reported for three complexes. (i) Tetrakis(1,3-diphenyltriazene)dicopper(II): C. M. Harris, B. F. Hoskins, and R. L. Martin, *J. Chem. Soc.*, 3728 (1959); A. K. Majumdar and S. C. Saka, *J. Indian Chem. Soc.*, **50**, 697 (1973); M. Corbett, B. F. Hoskins, N. J. McLeod, and B. P. O'Day, *Acta Crystallogr., Sect. A*, **28**, 576 (1972). (ii) Tetrakis(arylazo oxime)dicopper(II): S. Gupta, K. C. Kalia, and A. Chatravorty, *Inorg. Chem.*, **10**, 1534 (1971). (iii) Di-μ-5,7,7-trimethyl-4,8-diazaundec-4-ene-1,11-diolato-*ONN'O'*-dicopper(II) perchlorate: J. S. De Courcy, T. N. Waters, and N. F. Curtis, *J. Chem. Soc., Chem. Commun.*, 572 (1977).

(15) EPR spectroscopic data were obtained using a Brucker spectrometer.

(16) $|2(\mathrm{CuCl_2}) \subset \mathbf{1a}|$ crystallizes in the monoclinic space group $P2_1/c$ with a = 7.943 (2), b = 22.481 (6), c = 17.538 (5) Å; β = 100.97 (2)°; V = 3074.47 Å^3; ρ_m = 1.48 and ρ_c = 1.47 g cm^{-3}; Z = 4 formula units per cell. A total of 3150 independent nonzero reflections, measured on a Philips PW 1100 diffractometer, with $I > 3\sigma(I)$ were used in structure determination; $R_F = 0.048$ and $R_{wF} = 0.057$.

(17) For general reviews of doubly bridged compounds, see U. Casellato, P. A. Vigato, and M. Vidali, *Coord. Chem. Rev.*, **23**, 31 (1977).

(18) Several attempts have been made to correlate the magnetic properties of binuclear complexes with structural data. See W. E. Hatfield, *ACS Symp. Ser.*, **No. 5**, 108 (1974); I. G. Dance, *Inorg. Chim. Acta*, **9**, 77 (1974); V. H. Crawford, H. W. Richardson, J. R. Mason, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **15**, 2107 (1976); P. J. Hay, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **97**, 4884 (1975); O. Kahn and B. Briat, *J. Chem. Soc., Faraday Trans.*, **72**, 268, 1441 (1976); R. D. Harcourt and G. E. Martin, *ibid.*, **73**, 1 (1977); O. Kahn, B. Briat, and J. Galy, *J. Chem. Soc., Dalton Trans.*, 1453 (1977).

(19) J. A. Bertrand and F. T. Helm, *J. Am. Chem. Soc.*, **95**, 8184 (1973).

(20) In a recent paper, H. B. Gray et al. suggest that a multiply bridged dioxygen–copper center is a more attractive structural possibility for oxyhemocyanin: D. M. Dooley, R. A. Scott, J. Ellinghaus, E. I. Solomon, and H. B. Gray, *Proc. Natl. Acad. Sci. U.S.A.*, **75**, 3019 (1978).

(21) Laboratoire de Cristallochimie et de Chimie Structurale; Equipe de Recherche Associé au C.N.R.S. (E.R.A. No. 8).

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Fluoroxysulfate: A Powerful New Oxidant and Fluorinating Agent[1]

Sir:

In 1926 Fichter[2] observed that the passage of fluorine through aqueous solutions of sulfate or bisulfate led to the production in the solutions of a "vergängliches Oxidationsmittel", or "ephemeral oxidant", that was more powerfully oxidizing than peroxymonosulfate and that decomposed over the course of several hours. Fichter's work was largely ignored for many years, and his conclusions have recently been challenged.[3] However, we have repeated a number of his experiments and have generally confirmed his results. In addition, we have isolated the "ephemeral oxidant" in the form of its rubidium and cesium salts and have identified it as the fluoroxysulfate ion, SO_4F^-.

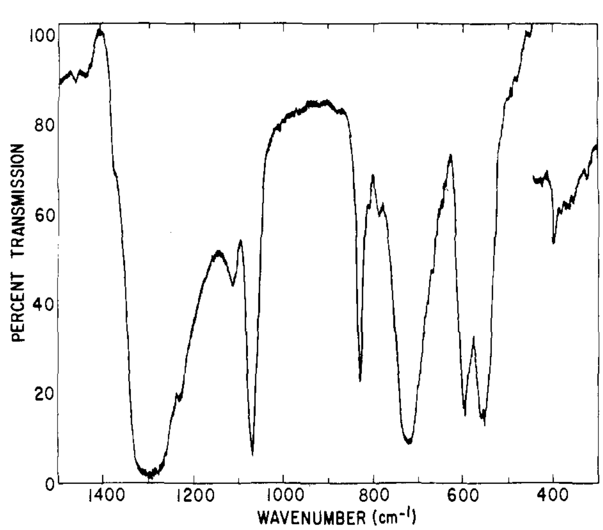

Figure 1. Infrared spectrum of $RbSO_4F$, taken with a Beckman IR 4260 spectrophotometer using a diamond anvil cell and a 4X beam condenser (ref 10). This technique was necessitated by the tendency of the fluoroxysulfates to react with KBr and AgCl infrared windows. The spectrum of $CsSO_4F$ is very similar, except that the band at 1105 cm^{-1} is considerably less prominent.

We prepared rubidium and cesium fluoroxysulfates by passing fluorine into solutions of Rb_2SO_4 and Cs_2SO_4, respectively. Approximately 20 mmol of F_2 (as a 20% mixture in nitrogen) was passed into 8 mL of 1.3 M Rb_2SO_4 or 2 M Cs_2SO_4 in a Tefzel tube over the course of an hour. An ice-salt bath was used to keep the solution temperature between 0 and −4 °C. The yellowish-white precipitates were centrifuged, washed with a little water, and dried in vacuo without heating. Yields were about 1 g of the rubidium salt and about 2 g of the cesium salt.

Samples for analysis were dissolved in water in Teflon bottles, and a slight excess of sodium carbonate was added. The solutions were then heated for 48 h at 90 °C to hydrolyze any fluorosulfate that might be present either as an impurity or as a decomposition product of the fluoroxysulfate.[4] Rubidium and cesium were determined by atomic absorption, fluoride with a fluoride-sensitive electrode, and sulfur gravimetrically as barium sulfate.[5] Anal. Calcd for $RbSO_4F$: Rb, 42.6; F, 9.5; S, 16.0. Found: Rb, 42.2; F, 8.8; S, 15.5. Calcd for $CsSO_4F$: Cs, 53.6; F, 7.7; S, 12.9. Found: Cs, 54.1; F, 7.3; S, 12.4. In addition, the oxidizing titers of the salts were determined by dissolving weighed amounts in a potassium iodide solution, acidifying, and titrating the liberated I_3^- immediately with standard thiosulfate solution. Results (mequiv/g): Calcd for $RbSO_4F$: 10.0. Found: 9.6. Calcd for $CsSO_4F$: 8.1. Found: 7.5. The salts contained an impurity that slowly oxidized iodide, thereby increasing the titer by 1–2%. The rate of this oxidation was unaffected by addition of molybdate, and we identify this impurity as peroxydisulfate.

The infrared and Raman spectra of the salts (Figures 1 and 2) agree well with those of the isoelectronic species ClO_4F[6-8] and its analogs ClO_4Cl[9] and ClO_4Br,[9] and they support the formulation of SO_4F^- as a fluoroxy ion or hypofluorite: O_3SOF^-. We assign the band at 830 cm^{-1} to the O-F stretch.

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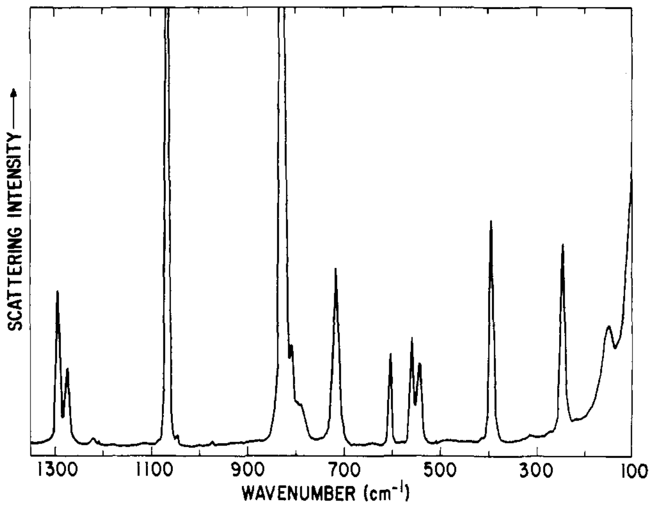

Figure 2. Raman spectrum of $RbSO_4F$. Excitation was with the 5145-Å line of a Coherent Radiation Model 52 argon ion laser. Measurements were made with a Spex 1401 monochromator linear in wavenumber and an RCA C31034 photomultiplier tube. Spectral slit width was approximately 5 cm^{-1}. The spectrum of $CsSO_4F$ is similar, except that only a single broad band is observed at 1280 cm^{-1}.

The fluorine-19 NMR spectra of $CsSO_4F$ and $RbSO_4F$ solutions in acetonitrile have been measured, using a Varian A-56/60 spectrometer. (Fluoroxysulfate is more stable in acetonitrile than in water.) With both salts a single line was observed at −132.3 ppm relative to $CFCl_3$. In contrast, an aqueous solution of KSO_3F gave a line at −37.5 ppm. These results provide further confirmation that the fluorine in SO_4F^- is bonded to oxygen rather than to sulfur, as it is in SO_3F^-. The isoelectronic $FClO_4$ has a resonance at −225.9 ppm.[6]

The solid salts appear to be fairly stable, although we have observed a slow loss of oxidizing power (ca. 3-5% per month). Heating to ca. 100 °C leads to a mild detonation, and mass spectrometric analysis of the gases evolved indicates O_2 to be the principal gaseous product, as expected for the reaction

$$MSO_4F \rightarrow MSO_3F + {}^1\!/_2O_2$$

Small amounts of SO_2F_2, SO_2, and SOF_2 are also formed. Thus an 18.9_2-mg sample of $RbSO_4F$ produced 0.0462 mmol of O_2 (calcd for $RbSO_4F$: 0.0472), along with 0.0073 mmol of SO_2F_2, 0.0011 mmol of SO_2, and 0.0002 mmol of SOF_2.

As Fichter reported, aqueous solutions of fluoroxysulfate are unstable. They decompose gradually, with the evolution of varying amounts of O_2. The acidity of the final solution is considerably lower than would result from the reaction

$$SO_4F^- + H_2O \rightarrow HSO_4^- + HF + {}^1\!/_2O_2$$

and it is likely that substantial quantities of SO_3F^- are formed. Variable amounts of two oxidizing species remain in solution after the decomposition. One reacts rapidly with I^- and is presumably peroxymonosulfate; the other reacts slowly with I^- unless molybdate is present and is presumably hydrogen peroxide. At 15 °C, the initial half-life of fluoroxysulfate in acid is around 30 min, but successive half-lives are shorter, probably because of the reaction of SO_4F^- with H_2O_2.

In alkaline solution the decomposition of fluoroxysulfate is essentially instantaneous. A transient yellow color is frequently observed, and a pungent odor is detected. Mass spectrometric analysis indicates the formation of O_2 mixed with small amounts of OF_2.

Also in agreement with Fichter's observations, aqueous solutions of fluoroxysulfate are very powerfully oxidizing. Chloride, bromide, and iodide are oxidized first to the free halogens and then to higher states. Vanadium(IV) is oxidized to vanadium(V), Ce(III) to Ce(IV), and Co(II) to Co(III). Manganous ion is oxidized first to Mn(III) and then to permanganate. Pb^{2+}, Tl^+, and Ag^+ are all oxidized. Surprisingly, chromium(III) is not oxidized in acidic solution, though in base chromate is formed. Fluoroxysulfate reacts vigorously with aqueous hydrazoic acid to produce a mixture of N_2, N_2O, and N_3F. In general, though not invariably, fluoroxysulfate is a considerably more rapid oxidant than peroxymonosulfate.

When toluene was shaken with aqueous fluoroxysulfate, the reaction products, as determined by gas chromatography-mass spectrometry, included fluorotoluenes and fluorobenzyl fluorides, cresols and fluorocresols, fluorobenzyl alcohol, and benzaldehyde. No nonaromatic products were observed.

Fluoroxysulfate is the first known example of an ionic hypofluorite. Its ionic character is of especial significance in that it permits the formation and isolation of relatively stable salts. The stability of these salts, along with their ease of preparation and unusual reactivity, may well make the fluoroxysulfates uniquely useful synthetic and analytical reagents for both inorganic and organic chemistry.

Note Added in Proof. Although the fluoroxysulfates do not ordinarily decompose violently, on two occasions the introduction of a spatula into a 100-mg sample of $CsSO_4F$ produced a sharp detonation. Caution is called for in the handling of larger quantities of these salts.

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References and Notes

(1) Work performed under the auspices of the Division of Basic Energy Sciences of the U.S. Department of Energy.
(2) Fichter, Fr.; Humpert, K. *Helv. Chim. Acta* **1926**, *9*, 602.
(3) Wannagat, U.; Horn, E. M.; Valk, G.; Höfler, F. *Z. Anorg. Allg. Chem.* **1965**, *340*, 181.
(4) Ryss, I. G.; Gribanova, T. A. *Zh. Fiz. Khim.* **1955**, *29*, 1822.
(5) Analyses carried out by Galbraith Labs., Knoxville, Tenn.
(6) Agahigian, H.; Gray, A. P.; Vickers, G. D. *Can. J. Chem.* **1962**, *40*, 157.
(7) Macheteau, Y.; Gillardeau, J. *Bull. Soc. Chim. Fr.* **1969**, 1819.
(8) Christe, K. O.; Curtis, E. C. Submitted for publication.
(9) Christe, K. O.; Schack, C. J.; Curtis, E. C. *Inorg. Chem.* **1971**, *10*, 1589.
(10) Ferraro, J. R.; Basile, L. J. *Am. Lab.*, **1979**, *11* (3), 31.

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The Enzymatic Conversion of Farnesyl to Nerolidyl Pyrophosphate: Role of the Pyrophosphate Moiety

Sir:

Since the introduction of the isoprene rule by Ruzicka in the early 1920s,[1] the acyclic sesquiterpene alcohol farnesol (**1a**) and its tertiary allylic isomer, nerolidol (**2a**), have played a prominent role in biogenetic speculations and related chemical model studies.[2] Although a great deal is now known about farnesyl pyrophosphate biosynthesis, the details of the formation and subsequent metabolism of nerolidol and its biologically activated ester, nerolidyl pyrophosphate (**2b**), remained obscure until only very recently.[3] As reported in previous communications,[4] using both intact cells and cell-free enzymes of *Gibberella fujikuroi*, we have demonstrated that the fungal sesquiterpene metabolite cyclonerodiol (**3b**) is

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