compound by the reaction of amidosulfuryl chloride and an alkali fluoride; Jonas and Voigt[2] allowed isocyanatosulfuryl chloride to react with an alkali fluoride to form isocyanatosulfuryl fluoride, which subsequently was hydrolyzed to amidosulfuryl fluoride. No yields have been reported on these methods, both of which require several steps to prepare the compound from commercially available products. In another route published by Appel and Eisenhauer[3] amidosulfuryl fluoride is said to be made by ammonolysis of disulfuryl fluoride. Again several additional steps or a pressure reaction are involved to prepare the very toxic intermediate in good yields.

We wish to report a new reaction which permits production of amidosulfuryl fluoride with high over-all yields by a simple two-step reaction from available materials. First sulfamic acid is allowed to react with phosphorus pentachloride to form the known trichlorophosphonitridosulfuryl chloride[4] (yields up to 95%). When treated with liquid anhydrous hydrofluoric acid, trichlorophosphonitridosulfuryl chloride undergoes reaction by which the P=N bond is cleaved. At the same time at least some of the chlorine atoms are substituted by fluorine, and amidosulfuryl fluoride is formed according to the reaction

$$Cl_3PNSO_2Cl + xHF \xrightarrow{BF_3} H_2NSO_2F + P(Cl,F)_5 + nHCl \qquad n = 1\text{–}4$$

Addition of some boron trifluoride is necessary to promote the reaction, suggesting a proton-catalyzed mechanism.

Amidosulfuryl fluoride is produced in yields up to about 70–75% and can be isolated in essentially pure form simply by distillation. Purer product is obtained by extraction of the reaction mixture with suitable organic solvents prior to distillation.

Attempts to prepare amidosulfuryl fluoride by reaction of trichlorophosphonitridosulfuryl chloride with anhydrous hydrofluoric acid alone, or by heating it with alkali fluorides in acetonitrile, did not produce the desired product.

Amidosulfuryl fluoride has been found to be sufficiently stable to be stored in glass containers for extended periods of time, if moisture is thoroughly excluded.

Experimental

Trichlorophosphonitridosulfuryl chloride (27 g., 0.108 mole), made by the method of Kirsanov,[4] was placed in a Teflon trap and about 30 ml. of anhydrous hydrofluoric acid and about 2–3 g. of boron trifluoride were condensed upon it. (A convenient way to liquefy hydrofluoric acid is to pass the gas through an ice-cooled copper coil.) The clear colorless solution formed was left at room temperature for 2.5 days protected from moisture. During this time there was evaporation of part of the hydrofluoric acid, together with hydrochloric acid and phosphorus halogenides produced as by-products. The rest of the low-boiling material (mainly HF) was stripped off at room temperature and about 5 mm. pressure. The residue was distilled in a small glass apparatus at reduced pressure to yield 8 g. (74% of theory) of crude product which melted at 5°. On redistillation at 3 mm. pressure the product distilled constantly at 70° (lit. b.p. 88° (12 mm.)) and melted at 6° (lit. m.p. 7–8°).

Anal. Calcd. for H_2FNO_2S: N, 14.1; S, 32.3; F, 19.1. Found: N, 13.2; S, 31.9; F, 18.3.

A pure sample of amidosulfuryl fluoride was obtained by washing crude reaction product first with benzene and subsequently extracting amidosulfuryl fluoride with chloroform prior to distillation. The sample so purified melted at 6–8°.

Anal. Calcd. for H_2FNO_2S: N, 14.1. Found: N, 14.1.

The compound has the following infrared absorption bands (cm.$^{-1}$): 3401 (s), 3311 (s), 1553 (m), 1410 (vs), 962 (m), 784 (vs).

Acknowledgment.—Analytical work was performed by our Analytical Department, including the interpretation of the infrared spectra by Miss Ruth A. Kossatz.

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[2] H. Jonas and D. Voigt, *Angew. Chem.*, **70**, 572 (1958).

[3] (a) R. Appel and B. Eisenhauer, *ibid.*, **70**, 742 (1958); (b) R. Appel and G. Eisenhauer, *Z. anorg. allgem. Chem.*, **310**, 90 (1961).

[4] A. V. Kirsanov, *Izv. Akad. Nauk SSSR*, 426 (1950).

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The Preparation and Structure of Anhydrous Bis(dipivaloylmethanido)iron(II)

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Studies of the physical properties of solvated and unsolvated β-diketone complexes of iron(II) are usually troubled[2] by the reactivity of the species with oxygen. Recent studies by Buckingham, *et al.*,[3] have shown that bis(2,4-pentanediono)iron(II) is high-spin (μ = 5.4 B.M. at room temperature) and has a limited room-temperature solubility (~1–2% w./v.) in nonpolar organic solvents such as benzene or toluene. It appears that the anhydrous $Fe(acac)_2$ exists as a weakly associated polymer in the solid state and in solution. Polymerization has been found previously with $Ni(acac)_2$,[4] $Co(acac)_2$[5,6] and $Mn(acac)_2$.[7]

With 2,2,6,6-tetramethyl-3,5-heptanedione(dipivaloylmethane) as the β-diketone, polymerization is prevented[8] and one forces the metal to assume a coordination number of four (or less) in the neutral bis complex. In the case of nickel(II) and copper(II), a planar molecule results, while with cobalt(II) and

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[1] (a) Case Institute of Technology; (b) Brown University.

[2] See, for example, D. A. Buckingham, J. L. E. Cheong, J. E. Fergusson, and C. J. Wilkins, *J. Chem. Soc.*, 3461 (1963). G. S. Hammond, D. C. Nonhebel, and C-H. S. Wu, *Inorg. Chem.*, **2**, 73 (1963), report an unsuccessful attempt to prepare $Fe(DPM)_2$.

[3] D. A. Buckingham and J. T. Henry, to be published.

[4] J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **84**, 24 (1962), and references therein.

[5] J. P. Fackler, Jr., *Inorg. Chem.*, **2**, 266 (1963).

[6] F. A. Cotton and R. H. Soderberg, *ibid.*, **3**, 1 (1964).

[7] D. P. Graddon and G. M. Mockler, *Australian J. Chem.*, **17**, 1119 (1964).

[8] F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **83**, 2818 (1961).

zinc(II), tetrahedral coordination of the metal is realized.[9]

Independent work in each of our laboratories has resulted in the preparation and characterization of bis(dipivaloylmethanido)iron(II), $Fe(DPM)_2$. This bright yellow material, which chars immediately on exposure to air, is isomorphous[9] with the tetrahedral (strictly D_{2d}) $Zn(DPM)_2$ and $Co(DPM)_2$ and thus is the first example of a tetrahedral iron(II) complex in which the metal is bonded to four oxygens. The room-temperature magnetic susceptibility of 5.0 B.M. confirms the presence of a spin-free $3d^6$ electron configuration and suggests a ^5E (in T_d) ground state. Attempts to observe the expected $^5T_2 \leftarrow {}^5E$ absorbance, which is found near 4000 cm.$^{-1}$ in $[FeCl_4]^{-2}$ species,[10] in reflectance spectra[11] were unsuccessful due to the presence of ligand overtones in the region in which the band should be found. The high-energy spectral cut-off for reflectance on the powdered solid appears near 10,000 cm.$^{-1}$. This suggests the presence of a low-energy electron-transfer band.

Experimental

Bis(2,2,6,6-tetramethyl-3,5-heptanediono)iron(II).—Ferrous sulfate (~1 g.) is dissolved in water (~15 ml.) to which one drop of sulfuric acid has been added. (The addition of acid prevents the slow formation of iron(III).) An excess of DPM is added to methanol (~30 ml.) and the two solutions are mixed, after exhaustive deoxygenation. A dilute aqueous solution of sodium hydroxide is added and, if oxygen has been rigorously excluded at all stages, a bright yellow precipitate is formed. The complex is washed free from traces of iron(III) by *n*-hexane, in which the $Fe(DPM)_3$ is very soluble. The bright yellow solid, which chars and smokes instantly when exposed to air, is dried under vacuum at room temperature.

Anal. Calcd. for $C_{22}H_{38}O_4Fe$: C, 62.6; H, 9.1; mol. wt., 422. Found: C, 62.4; H, 8.9; mol. wt. (cryoscopically in benzene), 418–435.

The magnetic susceptibility was determined at room temperature using the standard Gouy technique[12]: $\chi_g^{\text{uncor}} = 25.5 \times 10^{-6}$ c.g.s. unit at 20°, $\mu_{\text{eff}}^{\text{cor}} = 5.0$ B.M.

The X-ray powder pattern of the complex, sealed in a glass capillary, was observed with a Debye–Scherrer camera. The spacings of the first seven lines observed were (in Å.): 9.43 (s), 6.15 (m), 5.49 (w), 5.30 (w), 4.79 (m), 4.62 (s), 3.97 (w). Assuming the tetragonal cell constants[9] for $Zn(DPM)_2$, a = 10.67 Å., c = 21.76 Å., the first nine lines are calculated to be (*hkl* value in parentheses): 9.57 (011), 6.20 (112), 6.00 (013, vw), 5.43 (004), 5.34 (200), 4.79 (202), 4.66 (211), 4.03 (015), 3.99 (123). The X-ray powder photographs for the zinc(II), cobalt(II), and iron(II) complexes are nearly identical by a visual inspection.

Acknowledgment.—J. P. F. acknowledges support by the National Science Foundation, GP-196, for this work.

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[9] F. A. Cotton and J. S. Wood, *Inorg. Chem.*, **3**, 245 (1964).

[10] C. Furlani, E. Cervone, and V. Valenti, *J. Inorg. Nucl. Chem.*, **25**, 159 (1963).

[11] Reflectance spectra were observed with powdered specimens held in a special holder fabricated for use with the standard attachment for a DK-2 spectrophotometer.

[12] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p. 415.

Correspondence

Bond Angles in the Binuclear Molybdenum(VI) Complex Anion $[MoO_2(C_2O_4)(H_2O)]_2O^{-2}$

Sir:

The crystal structure of the compound $K_2\{[MoO_2(C_2O_4)(H_2O)]_2O\}$ has recently been reported by Cotton, Morehouse, and Wood[1] (CMW). It was found that the various Mo–O bond lengths and O–Mo–O bond angles varied considerably, and CMW stated that all of these variations appeared to correlate very well with simple considerations of interatomic repulsions and Mo–O bond orders. The six oxygen ligands of each molybdenum atom are of four types, namely, terminal, bridge, oxalate, and water, with respective Mo–O bond lengths[2] of 1.692–1.698, 1.874, 2.096–2.185, and 2.330 Å., and the bond angles range from 73.5 to 106.5°. In a short discussion of the bond angles, CMW noted that "the largest O–Mo–O angle is between the two terminal Mo–O bonds, which are the shortest ones. Because of the shortness of these *cis* Mo–O bonds, O · · · O repulsion tends to be large and is at least partially mitigated by expansion of the interbond angle." They also pointed out that the next largest angles are those between the terminal bonds and the bridge bond, and that the smallest angles (except in the chelate) are those between the very long $Mo–OH_2$ bond and its four *cis* neighbors.

This apparent correlation of the bond angles with the lengths of the two associated bonds has led us to make additional considerations of this interesting structure. The O · · · O distances associated with each of the bond angles were calculated. The results are presented in Table I. It is seen that although there is a wide variation among the bond angles, the O · · · O distances are, with the exception of the constrained oxalate group, rather similar. They average to 2.78 Å., a value equal, within experimental error, to twice the van der Waals radius[3] of 2.80 Å. The r.m.s. error in this average is 0.05 Å., or only slightly larger than the standard error of about 0.03 Å. in O · · · O distances. It would thus appear that the bond angles at the molybdenum atoms in the complex are

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[1] F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).

[2] These bond lengths, which were calculated with the lattice constants and positional parameters given by CMW (except that x of O_6 was taken as −0.0360 instead of +0.0360), differ by up to 0.012 Å. from the values in their paper. See their note which follows.

[3] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 260.