

The Reaction of Di-2-pyridyl Ketone with Antimony(III) Fluoride. Preparation, Properties, Mössbauer Spectrum and Crystal Structure of Difluoro(methoxydi-2-pyridylmethoxo-*NN'*O)antimony(III) †

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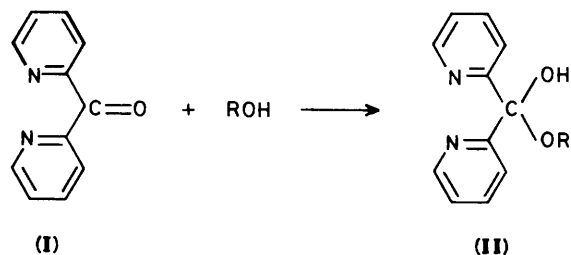
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Di-2-pyridyl ketone (dpk) reacts with SbF_3 in methanol undergoing nucleophilic addition from the solvent. The resultant antimony(III) complex $\text{SbF}_2[\text{OC}(\text{OMe})(\text{NC}_5\text{H}_4)_2]$, involving the carbinol form of dpk as a *fac*-terdentate N,N,O ligand, has been characterized by Mössbauer spectroscopy and single-crystal X-ray analysis. It crystallizes in the orthorhombic system, space group *Pnma*, with $a = 7.586(1)$, $b = 14.322(1)$, $c = 11.924(1)$ Å, and $Z = 4$. Least-squares refinement based on 710 observed reflections converged to $R = 0.036$ and $R' = 0.033$. The co-ordination polyhedron around Sb is a square pyramid [Sb-F 1.967(4), Sb-N 2.580(7), and Sb-O(1) 1.993(8) Å]. The molecule lies on a crystallographic mirror plane.

The interaction between di-2-pyridyl ketone (dpk) and metal ions (mainly transition-metal ions) has attracted considerable attention.¹⁻¹² Although dpk can potentially exhibit two modes of chelation, *i.e.* through the two pyridyl ring nitrogen atoms, or less likely through one ring nitrogen and the carbonyl oxygen, previous studies^{2-6,8-12} indicated that only N,N co-ordination occurs in a variety of complexes containing the dpk unit as such. Moreover, depending upon the experimental conditions, the reaction with dpk has often been reported to afford formally 'hydrated' or 'alcoholated' metal-dpk complexes,^{1-6,8,9,11,12} which do not show the characteristic ketonic group stretching in the i.r. spectrum. With these systems it was recognized^{2,3} that dpk, (I), undergoes a metal-promoted nucleophilic addition.



Besides retaining the possibility of acting as N,N-bidentate, the resulting carbinol form (II) should be considered also a potentially terdentate N,N,O ligand, and complexes of such terdentate systems have been proposed³ as possible intermediates in the metal-promoted reaction of the carbonyl group of dpk. None of the previous studies gave definite information about the structure of any metal-dpk complex.

During our investigations on a series of antimony(III) halide complexes with multidentate ligands, we observed that dpk reacts with antimony trifluoride in methanol undergoing nucleophilic addition from the solvent and affording, almost quantitatively, the compound $\text{SbF}_2[\text{OC}(\text{OMe})(\text{NC}_5\text{H}_4)_2]$.

Here we report on the crystal and molecular structure of this complex which substantiates for the first time the ability of (II) to act as a monoanionic terdentate ligand. The compound has been further characterized by ¹²¹Sb Mössbauer and i.r. spectroscopy.

Experimental

Preparation of $\text{SbF}_2[\text{OC}(\text{OMe})(\text{NC}_5\text{H}_4)_2]$.—Equimolar quantities of SbF_3 and dpk (2 mmol) were dissolved in methanol (20 cm³) at room temperature. After standing for a few days the solution afforded well formed crystals of the required compound (Found: C, 38.95; H, 3.05; N, 7.45. $\text{C}_{12}\text{H}_{11}\text{F}_2\text{N}_2\text{O}_2\text{Sb}$ requires C, 38.45; H, 2.95; N, 7.45%), m.p. 121–123 °C, $\Lambda = 7.0 \text{ S cm}^2 \text{ mol}^{-1}$ for a 1 mmol dm⁻³ solution in MeOH at 25 °C.

Spectroscopic Measurements.—The i.r. spectra (4 000–180 cm⁻¹) were recorded as Nujol or hexachlorobutadiene mulls between CsI plates using a Perkin-Elmer 580 spectrophotometer. Relevant bands (cm⁻¹): 1 595ms, 1 570mw [pyridyl ring, mixed $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{C})$]; 1 295w [in plane $\delta(\text{C}-\text{H})?$]; 763s [out-of-plane $\delta(\text{C}-\text{H})$]; 515ms, 480s [$\nu(\text{Sb}-\text{F})$]; 325mw, 268mw, and 245mw [$\nu(\text{Sb}-\text{O})$ and $\nu(\text{Sb}-\text{N})$].

The Mössbauer spectrum was obtained by cooling both the source (0.5 mCi $\text{Ca}^{121\text{m}}\text{SnO}_3$) and the absorber (12 mg Sb cm⁻²) at liquid-nitrogen temperature and using the apparatus and methodology previously described.¹³

X-Ray Structure Determination.—The crystal and refinement data are summarized in Table 1. The compound is in the form of transparent prisms stable to air. The X-ray intensity data were collected on a four-circle Siemens-Stoe automated diffractometer with graphite-monochromated Mo- K_α radiation. The unit-cell parameters were determined on the basis of 25 strong reflections obtained by mounting the crystal at random, varying the orientation angles θ and χ in a 120° range with the detector position varying between $\theta = 6$ and 10°. For the determination of precise lattice parameters 20 strong reflections with $10 < \theta < 15$ were considered.

The intensities of three standard reflections ($-1\ 2\ -2$; $3\ 2\ 6$;

† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

31–7) monitored at 100-min intervals showed no greater fluctuation than that expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects. The structure was solved using three-dimensional Patterson and Fourier techniques and refined by full-matrix least squares. Anisotropic thermal parameters were employed except for hydrogen atoms which were introduced at calculated positions (C–H 0.98 Å) with fixed isotropic $U = 0.06 \text{ \AA}^2$.

Anomalous dispersion for Sb was taken into account in the refinement, and atomic scattering factors were from ref. 14. Data processing and computations were carried out using the SHELX 76 program package.¹⁵ Final positional parameters are presented in Table 2.

Table 1. Crystal data

Formula	$C_{12}H_{11}F_2N_2O_2Sb$
M	376.99
Space group	$Pnma$
Crystal system	Orthorhombic
$a/\text{\AA}$	7.586(1)
$b/\text{\AA}$	14.322(1)
$c/\text{\AA}$	11.924(1)
$U/\text{\AA}^3$	1 295.5
Z	4
$D_c/\text{Mg m}^{-3}$	1.93
$F(000)$	728
Radiation ($\lambda/\text{\AA}$)	0.710 69
Reflections measured	1 200
Scan method	ω/θ
Scan speed/ $^\circ \text{ min}^{-1}$	1.20
Scan width/ $^\circ$	1.20
Background counts per s of counting time	10
$2\theta_{\text{max}}/^\circ$	50
Reflections observed [$I \geq 3\sigma(I)$]	710
Weighting scheme, w	$2.5432[\sigma^2(F_o) + 0.000 104(F_o)^2]^{-1}$
$R = (\sum[F_o - F_c]/\sum F_o)$	0.036
$R' = [\sum w(F_o - F_c)^2/\sum w F_c ^2]^{\frac{1}{2}}$	0.033
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	19.8

Discussion

The structure consists of discrete molecules as shown in Figure 1, each lying in a crystallographic mirror plane; in this way the asymmetric unit is half a molecule. The mirror plane bisects the molecule through Sb, O(1), and C(1); the methoxy group [O(2) and C(2)] is somewhat out of the mirror plane with a statistical disposition of 50%. A perspective view of the molecule with the atom numbering scheme is shown in Figure 2 (only one of the two alternative positions of the methoxy group is represented; primed atoms are related to unprimed through the crystallographic mirror plane at $x, \frac{1}{2} - y, z$). The bond distances and angles are reported in Table 3.

The co-ordination polyhedron around Sb is a square pyramid, the base of which is formed by two fluorines and two nitrogens of the two pyridyl moieties (mirrored in pairs) and the apical position is occupied by the 'ketone' oxygen. The ligand $(H_4C_5N)_2C(OMe)O^-$, originating from dpk, is thus acting as *fac*-terdentate with fairly narrow N–Sb–O(1) [mirrored by N'–Sb–O(1)] and N–Sb–N' 'bite' angles of 68.2(2) and 75.5(3) $^\circ$, respectively. The Sb atom is 0.478(1) Å below the basal plane opposite the apical O(1) atom, which is 1.449(8) Å above.

Table 2. Fractional atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Sb	1 199(1)	2 500	3 093(1)
O(1)	–979(9)	2 500	4 027(5)
C(1)	–763(2)	2 500	5 196(1)
O(2)*	–2 409(1)	2 178(6)	5 720(9)
C(2)*	–3 852(2)	2 770(1)	5 409(2)
F	21(7)	1 541(3)	2 180(4)
N	1 478(11)	1 397(5)	4 795(6)
C(7)	1 099(28)	390(12)	6 710(12)
C(8)	2 284(24)	152(9)	5 943(13)
C(9)	2 483(16)	668(7)	5 003(10)
C(10)	270(12)	1 639(6)	5 535(7)
C(6)	76(16)	1 136(10)	6 520(9)

* Population parameter 0.5.

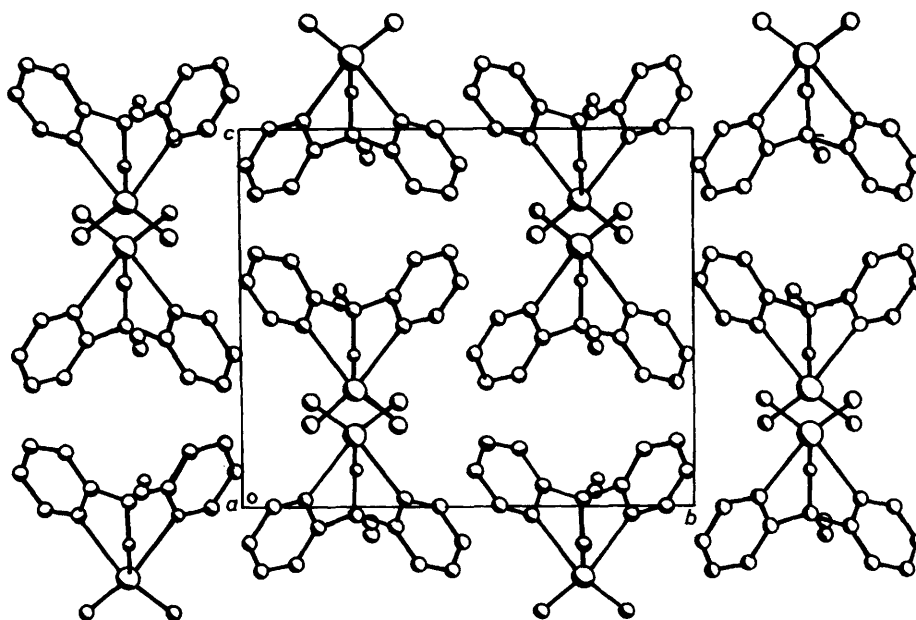
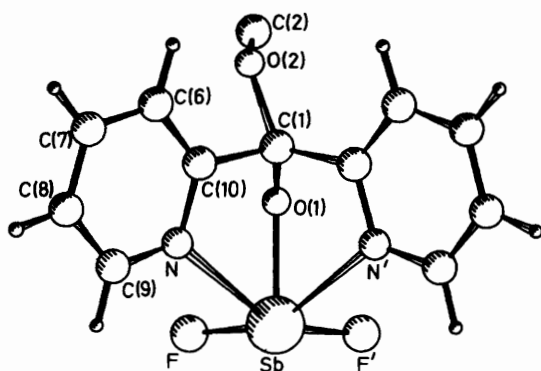


Figure 1. Packing diagram viewed down a

Table 3. Bond distances (Å) and angles (°)

Sb-F	1.967(4)	C(7)-C(6)	1.34(2)
Sb-N	2.580(7)	C(6)-C(10)	1.38(1)
Sb-O(1)	1.993(8)	C(1)-C(10)	1.52(1)
N-C(9)	1.32(1)	C(1)-O(1)	1.40(1)
N-C(10)	1.32(1)	C(1)-O(2)	1.47(1)
C(9)-C(8)	1.35(2)	O(2)-C(2)	1.43(2)
C(8)-C(7)	1.33(2)		
F-Sb-F'	88.5(3)	C(8)-C(7)-C(6)	119(1)
N-Sb-N'	75.5(3)	C(7)-C(6)-C(10)	120(1)
F-Sb-N	92.6(2)	C(9)-N-C(10)	118.9(9)
F-Sb-N'	154.2(2)	C(6)-C(10)-C(1)	126(1)
F-Sb-O(1)	86.1(2)	N-C(10)-C(1)	113.2(8)
N-Sb-O(1)	68.2(2)	C(10)-C(1)-O(1)	109.0(7)
Sb-N-C(9)	133.0(8)	C(10)-C(1)-O(2)	94.1(6)
Sb-N-C(10)	108.0(5)	O(1)-C(1)-O(2)	108.8(9)
Sb-O(1)-C(1)	117.3(7)	C(10)-C(1)-C(10')	108.9(9)
N-C(9)-C(8)	122(1)	C(1)-O(2)-C(2)	130(1)
C(9)-C(8)-C(7)	120(1)	C(6)-C(10)-N	120(1)

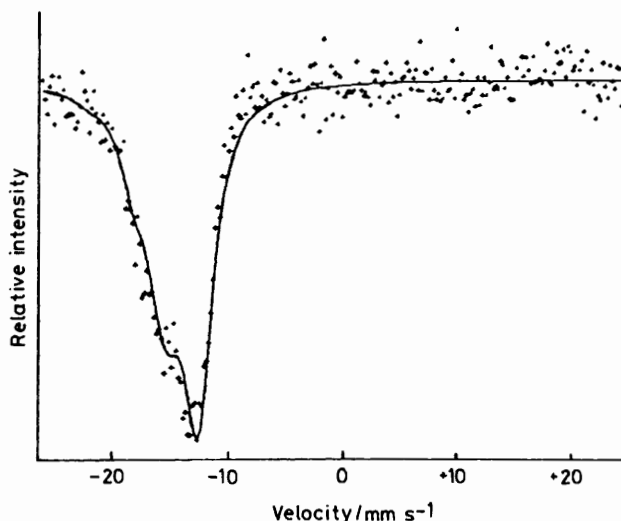
**Figure 2.** Perspective view of a molecule of the complex with the atom numbering scheme

The lone electron pair is assumed to lie *trans* to the Sb-O(1) bond. The displacement is larger than that observed in the compound $\text{SbF}_3[\text{ONC}_5\text{H}_4(\text{OMe-4})]_2 \cdot \text{H}_2\text{O}$ ¹⁶ which has a similar pyramidal geometry in which the antimony atom lies 0.29 Å above the bond plane formed by a O_2F_2 grouping of donor atoms.

The Sb-F distance [1.968(7) Å] is equal to that reported for Sb-F(basal) in $\text{SbF}_3[\text{ONC}_5\text{H}_4(\text{OMe-4})]_2 \cdot \text{H}_2\text{O}$ ¹⁶ [1.968(5) Å] and in $\text{SbF}(\text{O}_2\text{C}_6\text{H}_4)(\text{phen})$ ¹⁷ [1.965(7) Å], and intermediate between the values ranging from 1.938(2) to 1.997(2) Å observed in $\text{SbF}_3(\text{phen})(\text{tu})$ ¹⁸ ($\text{C}_6\text{H}_4\text{O}_2^{2-}$ = pyrocatecholate dianion, phen = 1,10-phenanthroline, and tu = thiourea).

The Sb-N bond distance [2.584(7) Å] can be compared with those observed for the phen ligand which is chelating asymmetrically to the antimony(III) atom in $\text{SbF}(\text{O}_2\text{C}_6\text{H}_4)(\text{phen})$ [2.448(9) and 2.569(9) Å],¹⁷ in the cationic species containing two phen units [$\text{Sb}(\text{O}_2\text{C}_6\text{H}_4)(\text{phen})_2$]⁺ [2.423(7), 2.592(5), and 2.467(7), 2.694(5) Å, respectively],¹⁹ in $\text{SbF}_3(\text{phen})(\text{tu})$ [2.556(6) and 2.731(3) Å]¹⁸ as well with the less geometrically constrained Sb-N distances of 2.53 and 2.64 Å found in SbCl_3 complexes of aniline.²⁰

It is of interest that the value of the Sb-O(1) bond distance [1.990(8) Å] *trans* to the assumed site of the lone pair is comparable to the value [2.007(8) Å] found for Sb-O *trans* to the lone pair in $\text{SbF}(\text{O}_2\text{C}_6\text{H}_4)(\text{phen})$.¹⁷ Taking also into account that in $\text{SbF}_3[\text{ONC}_5\text{H}_4(\text{OMe-4})]_2 \cdot \text{H}_2\text{O}$ ¹⁶ the Sb-F(apical) distance is particularly short, 1.905(5) Å, it seems that the

**Figure 3.** The Mössbauer spectrum of $\text{SbF}_2[\text{OC}(\text{OMe})(\text{NC}_5\text{H}_4)_2]$

observation of a shortening of Sb-X bond distances *trans* to the lone-pair position²¹ is valid for these pyramidal SbX_5E antimony(III) species. This assumption was not verified for $\text{SbF}_3(\text{phen})(\text{tu})$ ¹⁸ where the interaction with an additional donor atom (a sulphur of the thiourea molecule at large distance) modifies the lone-pair position which is no longer really *trans* to a particular Sb-X bond.

The geometry of the ligand appears normal. The two planar pyridyl moieties are inclined to each other at 75.1(3)° (dihedral angle) and 118.4(3)° with respect to the co-ordination square plane. The bond lengths around the sp^3 -hybridized carbon atom C(1) are normal for single C-C [C(1)-C(10) 1.51(1) Å] and C-O [C(1)-O(1) 1.40(1) and C(1)-O(2) 1.46(2) Å], while the angles C(10)-C(1)-O(2) and C(10')-C(1)-O(2) deviate noticeably from regular tetrahedral values, being 93.2(5)° and 124.4(5)°, respectively. The Sb-O(1)-C(1) angle [117.3(3)°] is indicative of a possible sp^2 hybridization of the oxygen atom. Previous observations on Sb-O and Sb-N bond distances indicate that antimony(III) fits fairly well into the terdentate N,N,O system. However, the present ligand appears somewhat 'strained' as judged from the asymmetry of the angles (those external to the pyridyl ring) at C(10) and N: C(1)-C(10)-C(6) 126(1), C(1)-C(10)-N 113.2(8), Sb-N-C(10) 108.0(5), and Sb-N-C(9) 133.0(9)°. However, despite the above distortions, Sb lies sensibly in the plane of the pyridyl ring.

Spectroscopic Data.—The alcoholysis of dpk is reflected in the disappearance of the ketonic $\nu(\text{C}=\text{O})$ band from the i.r. spectrum of the present compound (see Experimental section). The spectrum also shows an increase in the pyridyl-ring mixed C=N and C=C stretching frequencies (1 578s and 1 565m cm^{-1} for free dpk), as well as in the $\delta(\text{C}-\text{H})$ out-of-plane modes (753s and 742s cm^{-1} for free dpk) previously observed for metal complexes of both dpk and its 'reacted' forms.¹⁻¹² A distinctive feature of previously reported data^{6,12} is the considerable reduction in intensity of the $\delta(\text{C}-\text{H})$ in-plane modes (1 325s cm^{-1} for free dpk). In the skeletal region, whereas the asymmetric and symmetric SbF stretchings can easily be assigned, a clear distinction between $\nu(\text{Sb}-\text{N})$ and $\nu(\text{Sb}-\text{O})$ modes cannot be made.

The Mössbauer spectrum of the compound is shown in Figure 3 together with the calculated one corresponding to the best fitted parameters: isomer shift (i.s.) (relative to the source) = -15.2 mm s^{-1} , eQV_{zz} = 19.5 mm s^{-1} , and $\eta < 0.2$. These values may be compared with those measured for SbF -

(O₂C₆H₄)(phen) and [Sb(O₂C₆H₄)(phen)₂]⁺ (i.s. = -14.3 and -14.0; eQV_{zz} = 15.4 and 16.1 mm s⁻¹, respectively¹⁹) where Sb^{III} is co-ordinated by second-row donor atoms and crystallographic data^{17,19} also show the presence of a stereochemically active lone pair. Also of interest are the parameters reported²² for SbF₃ (i.s. = -14.8, eQV_{zz} = 19.1 mm s⁻¹). The structure of the latter²³ consists of SbF₃ pyramidal units, with short Sb-F bonds nearly at right angles, and three additional Sb...F contacts providing an overall C_{3v} symmetry. The lone pair can be assumed to lie opposite to the three short SbF bonds along the C_{3v} axis.

We think that the SbF₃ and SbF₂O units found in antimony trifluoride and in the present compound respectively are essentially similar but in the latter the reduced symmetry results in a lone pair probably located roughly opposite to the oxygen atom. Although this could result in a non-zero value of the electric-field-gradient asymmetry parameter, η, the small contribution from the Sb-F or Sb-O bonds with respect to that from the lone-pair electron density in our opinion justifies the very small η value estimated from the fitting procedure.

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