Fluoro derivatives of bis(salicylideneaminato-*N*,*O*)copper(II) and -oxovanadium(IV)

John Burgess, John Fawcett,* Vitor Palma† and Syeda R. Gilani

Department of Chemistry, University of Leicester, Leicester LE1 7RH, England
Correspondence e-mail: jxf@leicester.ac.uk

The structures of five complexes of fluorine-containing bidentate salicylideneamine Schiff base ligands are reported. These are the bis-ligand copper(II) complexes of the Schiff bases derived from salicylaldehyde and 4-fluoro-, [Cu(C$_{13}$H$_9$FNO)$_2$], 3-fluoro-4-methyl-, [Cu(C$_{14}$H$_{11}$FNO)$_2$], 3,5-bis(trifluoromethyl)-, [Cu(C$_{15}$H$_8$F$_6$NO)$_2$], and 4-trifluoromethoxyanilines, [Cu(C$_{14}$H$_9$F$_3$NO$_2$)$_2$], and the bis-ligand oxovanadium(IV) complex of the Schiff base derived from salicylaldehyde and 4-trifluoromethoxyaniline, [VO(C$_{14}$H$_9$F$_3$NO$_2$)$_2$]. Three of the copper complexes have square-planar coordination at the metal, imposed by the virtue of symmetry, but the immediate coordination environment of the copper in the 3,5-bis(trifluoromethyl) complex is intermediate between square planar and tetrahedral. The coordination environment at the metal of the vanadium complex can be described as distorted square pyramidal.

Comment

Bidentate Schiff base ligands of various types and their metal complexes have been extensively studied for many decades. Of the various classes of Schiff base which can be generated by condensation of different types of amines and carbonyl compounds, one of the most popular has been that of the salicylideneamines, potential *O*,*N*-donors derived from (substituted) salicylaldehydes and primary amines. If the amine is aromatic, then a great variety of ligands can be prepared from the great range of substituted anilines which are available. We are interested in the synthesis of fluoro-substituted ligands and metal complexes, in particular in relation to the consequences of fluorine-for-hydrogen replacement on solvation and on reactivity. Here we combine our specific interest in fluoro-derivatized complexes with our general interest in Schiff base complexes, reporting the preparations and structures of bis-ligand copper(II) complexes of the Schiff bases derived from salicylaldehyde

† Erasmus student visitor from CEQUP, Faculdade de Ciencias, Porto 4150, Portugal.

and 4-fluoro-, (I), 3-fluoro-4-methyl-, (II), 3,5-bis(trifluoromethyl)-, (III), and 4-trifluoromethoxyanilines, (IV), and the bis-ligand oxovanadium(IV) complex of the Schiff base derived from salicylaldehyde and 4-trifluoromethoxyaniline, (V).
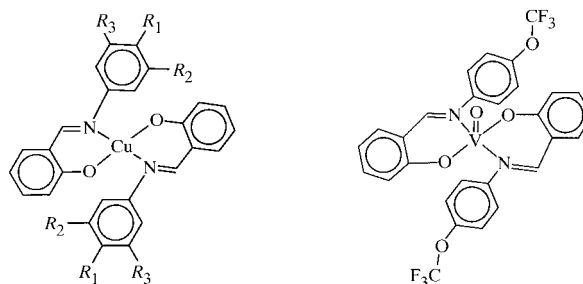
(I) R_1=F; R_2, R_3=H
(II) R_1=Me; R_2=F; R_3=H
(III) R_1=H; R_2, R_3=CF$_3$
(IV) R_1=OCF$_3$; R_2, R_3=H

(V)

For the copper complexes (I), (II) and (IV), the Cu atom and the four ligand donor atoms are coplanar, as expected. However, the 3,5-CF$_3$-substituted complex (III) has a distorted coordination at the Cu atom, intermediate between square-planar and tetrahedral, with an interplanar angle (Cu1—O1—N1 to Cu1—O1′—N1′) of 37.8 (1)°. Such distortion may be compared with that engendered by the attachment of relatively bulky groups to the N-donor atoms. This distortion has been of considerable interest to kineticists (Voss *et al.*, 1979). It has been tracked through X-ray diffraction structure determination of, for example, the *N-tert*-butyl derivative, where the angle between the mean planes of the chelate rings is 61.9° (Cheeseman *et al.*, 1966*a*) and through electronic spectroscopy (Cheeseman *et al.*, 1966*b*; Voss *et al.*, 1974). For all the Cu complexes, the substituted amine ring of each ligand is rotated about the N1—C8 bond from the
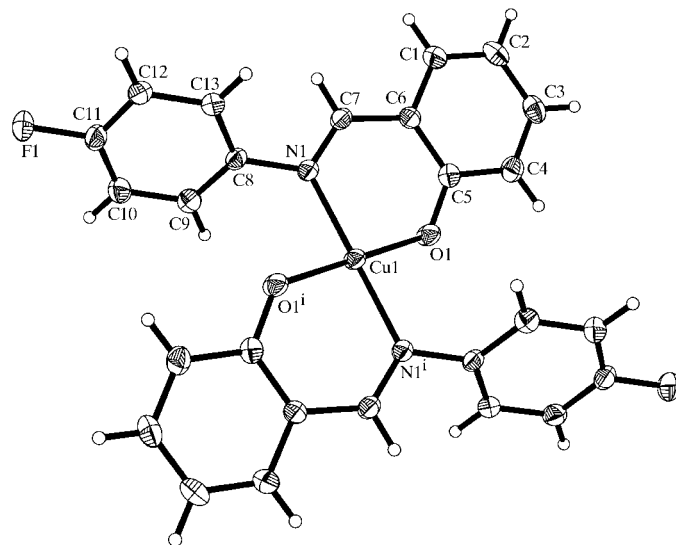

Figure 1
The molecular structure of one of the unique molecules of (I) showing the atom-numbering scheme and 30% probability displacement ellipsoids. H atoms are drawn as spheres of arbitary radii. [Symmetry code: (i) −*x*, −*y*, −*z*.]

salicylaldehyde plane. The interplanar angles between these rings are in the range 31.7 (2)° in (II) to 64.3 (1)° in (III). There is no apparent correlation between these angles and the bulk of the respective substituents on the amine-derived moieties of the Schiff base ligands.

Complexes (II), (III) and (IV) all exhibit disorder at the F-atom sites. The F atom of complex (II) was found to be disordered (50:50) between the sites resulting from the possible rotation configurations at the C—N bond. For both complexes (III) and (IV), the F atoms of the CF_3 groups were found to be disordered (50:50) between the two sites staggered by rotation about, respectively, the C—C or the C—O bond. In both cases, the disordered F atoms have high displacement parameters.

Metal–ligand donor-atom bond distances for the copper(II) complexes are summarized in Table 1, which also includes the results of an early structure determination of the unsubstituted parent complex (Baker *et al.*, 1966). Complex (I) has two unique molecules in the triclinic unit cell, and for both molecules, the Cu atom is located on a centre of symmetry. The Cu—O bond distances in three of our complexes are the same within experimental uncertainty, but are significantly less in the 3,5-bis(trifluoromethyl) complex. The same can be said of the Cu—N distances. These bond shortenings presumably reflect a small but significant increase in overall bond strength caused by the strongly electron-withdrawing CF_3 groups. Metal–ligand bond distances in the four substituted complexes appear to be marginally shorter (Cu—O) or marginally longer (Cu—N) than in the unsubstituted complex, though the low precision of the structure of the latter makes comparisons risky.

The Cu—O distances in the salicylideneaniline complexes are similar to those in other *O*-donor complexes of copper(II). However, they are slightly but significantly shorter than those to coordinated oxalate in, for example, the $[Cu(ox)_2]^{2-}$ anion [Cu—O = 1.933 (5) and 1.939 (5) Å; Bloomquist *et al.*, 1981] or in the uncharged ternary complexes [Cu(bipy)(ox)] [Cu—O =
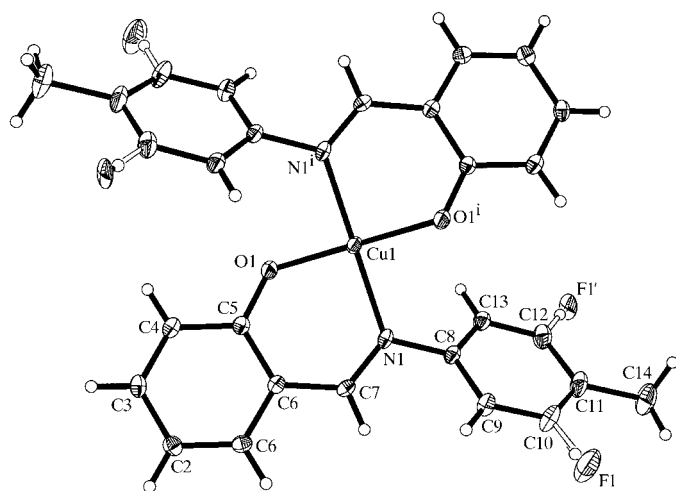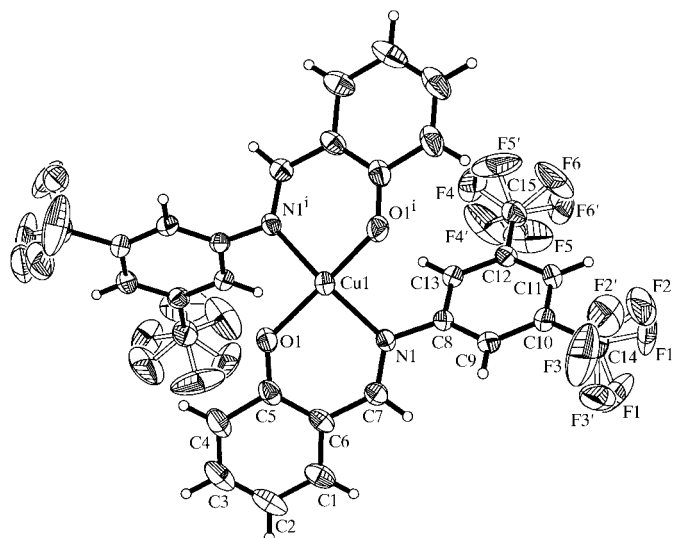

Figure 3
The molecular structure of (III) showing the atom-numbering scheme and 30% probability displacement ellipsoids. Open bonds indicate disordered F-atom sites. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

1.984 (4) and 1.992 (3) Å; Fitzgerald *et al.*, 1982] or [Cu(*N,N*-dimethylethane-1,2-diamine-*N*-oxide)(ox)(H₂O)] [Cu—O$_{ox}$ = 1.960 (4) and 1.965 (5) Å; Pajunen & Nasakkala, 1980], or to the closest water molecules in $Cu^{2+}_{(aq)}$ in various crystal hydrates and in aqueous solution (Cu—O = 1.93–2.00 Å; Mani & Rameseshan, 1961; Richens, 1997; Burgess, 1999). Cu—N distances are probably marginally shorter than in various ternary copper amines also containing coordinated halide or water (Cu—N = 2.03–2.05 Å; Colquhoun *et al.*, 1981; Hathaway & Billing, 1970).

The coordination environment at the metal of the vanadium complex (V) could be described as distorted square pyramidal or distorted trigonal bipyramid. In the square-pyramidal case, atoms O1, O1*A*, N1 and N1*A* form a plane (maximum deviation 0.186 Å for O1*A*) with the V atom 0.59 Å above this plane and the terminal O3 atom axial. In the trigonal bipyramid, the equatorial plane atoms are V1, O1, O1*A* and O3 (maximum deviation 0.0235 Å for V1) with N1 and N1*A* approximately axial (N1—V1—N1*A* 157.4°). The V—O and

Figure 2
The molecular structure of (II) showing the atom-numbering scheme and 30% probability displacement ellipsoids. Open bonds indicate disordered F-atom sites. [Symmetry code: (i) $-x, -y, -z$.]
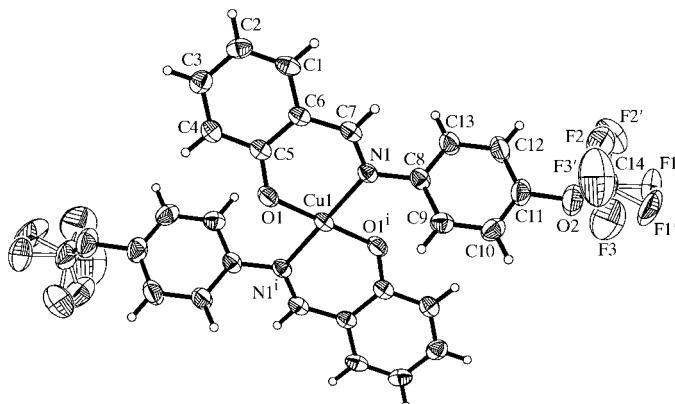

Figure 4
The molecular structure of (IV) showing the atom-numbering scheme and 30% probability displacement ellipsoids. Open bonds indicate disordered F-atom sites. [Symmetry code: (i) $-x, 1 - y, -z$.]

V—N distances in the vanadyl complex are V—O$_{ax}$ = 1.589 (2), V—O$_{eq}$ = 1.891 (2) and 1.904 (2), and V—N = 2.110 (2) and 2.121 (3) Å. These V—O distances may be compared with those in the penta- and hexahydrates of vanadyl sulfate, V—O$_{ax}$ = 1.586 (2) and 1.591 (5) Å and V—O$_{eq}$ = 2.004 (4) to 2.048 (5) Å (Ballhausen *et al.*, 1968; Tachez & Théobald, 1980*a*,*b*).

Intra-ligand bond distances for the chelate rings of the copper and oxovanadium complexes of the 4-OCF$_3$-substituted ligand are compared with their equivalents in the free ligand in Table 2. This shows that the C—O bond contracts significantly on complexation, consistent with a slight increase in double-bond character. However, there is no significant shortening of the extra-cyclic C—C bond, as is sometimes observed on chelation (it is already considerably closer to C—C in an aromatic ring than to an aliphatic C—C single bond). On the other hand, the C—N bond joining the aniline-derived nitrogen to its phenyl ring lengthens by a small but significant amount on complexation.
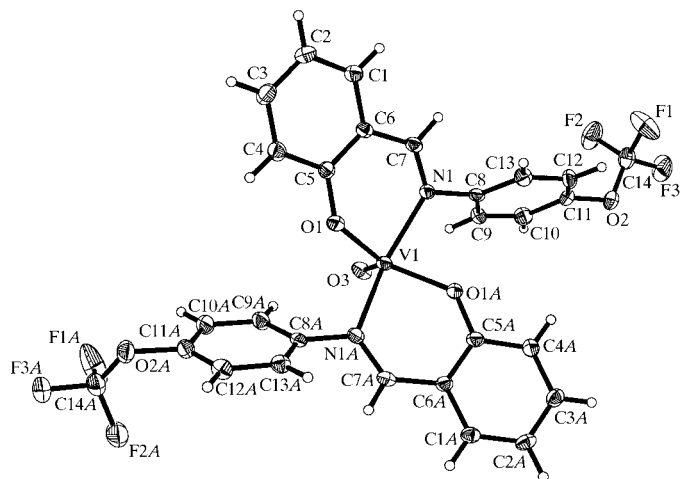

Figure 5
The molecular structure of (V) showing the atom-numbering scheme and 30% probability displacement ellipsoids.

Experimental

For the copper complexes, a solution of copper acetate (1 mmol) in a 50% ethanol–water mixture (10 ml) was added to a hot solution of salicylaldehyde (1 mmol) and the appropriate aniline (1 mmol) in ethanol (20 ml). Precipitation occurred immediately. The reaction mixtures were cooled, filtered and washed with ethanol and recrystallized from CHCl$_3$. The procedure for the vanadium complex was identical except for starting with vanadyl sulfate (1 mmol).

Compound (I)

Crystal data

[Cu(C$_{13}$H$_9$FNO)$_2$]
$M_r = 491.96$
Triclinic, $P\bar{1}$
$a = 9.995$ (2) Å
$b = 10.462$ (2) Å
$c = 10.569$ (2) Å
$\alpha = 95.13$ (2)°
$\beta = 92.48$ (2)°
$\gamma = 105.23$ (2)°
$V = 1059.5$ (4) Å^3

$Z = 2$
$D_x = 1.542$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
$\theta = 5.34–12.95°$
$\mu = 1.075$ mm^{-1}
$T = 190$ (2) K
Block, red
$0.48 \times 0.24 \times 0.23$ mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: analytical (*XPREP*; Sheldrick, 1997)
$T_{min} = 0.766$, $T_{max} = 0.810$
4119 measured reflections
3722 independent reflections
2994 reflections with $I > 2\sigma(I)$

$R_{int} = 0.027$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 11$
$k = -12 \rightarrow 11$
$l = -12 \rightarrow 12$
3 standard reflections
every 100 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.115$
$S = 1.095$
3722 reflections
301 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 1.4057P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.32$ e Å^{-3}

Compound (II)

Crystal data

[Cu(C$_{14}$H$_{11}$FNO)$_2$]
$M_r = 520.02$
Orthorhombic, $Pbca$
$a = 10.752$ (1) Å
$b = 7.893$ (1) Å
$c = 27.391$ (3) Å
$V = 2324.6$ (4) Å^3
$Z = 4$
$D_x = 1.486$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 44 reflections
$\theta = 4.71–12.41°$
$\mu = 0.985$ mm^{-1}
$T = 150$ (2) K
Block, red–brown
$0.58 \times 0.43 \times 0.34$ mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: analytical (*XPREP*; Sheldrick, 1997)
$T_{min} = 0.656$, $T_{max} = 0.777$
2677 measured reflections
2026 independent reflections
1452 reflections with $I > 2\sigma(I)$

$R_{int} = 0.035$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 12$
$k = -1 \rightarrow 9$
$l = -32 \rightarrow 1$
3 standard reflections
every 100 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.121$
$S = 1.013$
2026 reflections
169 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 4.1273P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Compound (III)

Crystal data

[Cu(C$_{15}$H$_8$F$_6$NO)$_2$]
$M_r = 727.98$
Monoclinic, $C2/c$
$a = 14.607$ (2) Å
$b = 7.423$ (1) Å
$c = 27.109$ (2) Å
$\beta = 98.07$ (1)°
$V = 2910.3$ (6) Å^3
$Z = 4$

$D_x = 1.662$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 39 reflections
$\theta = 5.38–12.61°$
$\mu = 0.860$ mm^{-1}
$T = 290$ (2) K
Block, red–brown
$0.47 \times 0.36 \times 0.33$ mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: ψ scan (*XEMP*; Sheldrick, 1997)
$T_{min} = 0.761$, $T_{max} = 0.838$
3159 measured reflections
2566 independent reflections
2013 reflections with $I > 2\sigma(I)$

$R_{int} = 0.015$
$\theta_{max} = 25.0°$
$h = -1 \rightarrow 17$
$k = -1 \rightarrow 8$
$l = -32 \rightarrow 31$
3 standard reflections
every 100 reflections
intensity decay: <2%

metal-organic compounds

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.096$
$S = 1.039$
2566 reflections
267 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 1.4869P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}

Compound (IV)

Crystal data

$[Cu(C_{14}H_9F_3NO_2)_2]$
$M_r = 623.98$
Monoclinic, $P2_1/c$
$a = 14.768\,(1)$ Å
$b = 10.663\,(1)$ Å
$c = 8.320\,(1)$ Å
$\beta = 95.87\,(1)°$
$V = 1303.3\,(2)$ Å^3
$Z = 2$

$D_x = 1.590$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
$\theta = 5.39–12.96°$
$\mu = 0.919$ mm^{-1}
$T = 290\,(2)$ K
Plate, red
$0.59 \times 0.49 \times 0.18$ mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: ψ scan ($XEMP$; Sheldrick, 1997)
$T_{min} = 0.678$, $T_{max} = 0.880$
3579 measured reflections
2684 independent reflections
1877 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
$\theta_{max} = 26.5°$
$h = -18 \rightarrow 18$
$k = -13 \rightarrow 1$
$l = -1 \rightarrow 10$
3 standard reflections
every 100 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.140$
$S = 1.028$
2684 reflections
214 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0808P)^2 + 0.2587P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.034$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Compound (V)

Crystal data

$[VO(C_{14}H_9F_3NO_2)_2]$
$M_r = 627.38$
Monoclinic, $P2_1/c$
$a = 27.392\,(3)$ Å
$b = 10.048\,(2)$ Å
$c = 9.654\,(1)$ Å
$\beta = 94.84\,(1)°$
$V = 2647.6\,(7)$ Å^3
$Z = 4$

$D_x = 1.574$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 39 reflections
$\theta = 4.81–12.52°$
$\mu = 0.460$ mm^{-1}
$T = 190\,(2)$ K
Block, orange
$0.56 \times 0.28 \times 0.22$ mm

Data collection

Bruker $P4$ diffractometer
ω scans
5407 measured reflections
3996 independent reflections
3138 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 24.0°$

$h = -31 \rightarrow 31$
$k = -11 \rightarrow 1$
$l = -1 \rightarrow 10$
3 standard reflections
every 100 reflections
intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.108$
$S = 1.034$
3995 reflections
379 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0466P)^2 + 1.4703P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

Table 1
Cu—O and Cu—N bond lengths (Å) in copper(II) complexes of (substituted) salicylideneanilines.

Substituent	Cu—O		Cu—N	
4-F	1.880 (2)	1.886 (3)	2.009 (3)	2.009 (3)
3-F,4-CH$_3$	1.884 (2)		2.017 (3)	
3,5-(CF$_3$)	1.869 (2)		1.969 (2)	
4-OCF$_3$	1.877 (2)		2.018 (2)	
unsubstituted	1.91		1.90	

Table 2
Selected intra-ligand bond distances (Å) in the 4-OCF$_3$ ligand and its complexes.

Bond	O1—C5	C5—C6	C6—C7	C7—N1	N1—C8
Ligand	1.350 (8)	1.403 (8)	1.440 (8)	1.289 (7)	1.415 (7)
Cu^{2+} complex	1.309 (4)	1.414 (4)	1.430 (4)	1.291 (4)	1.434 (4)
VO^{2+} complex	1.317 (3)	1.411 (4)	1.433 (4)	1.295 (4)	1.441 (3)
	1.308 (3)	1.405 (4)	1.433 (4)	1.297 (4)	1.439 (4)

For all compounds, data collection: $XSCANS$ (Fait, 1991); cell refinement: $XSCANS$; data reduction: $XSCANS$; program(s) used to solve structure: $SHELXS97$ (Sheldrick, 1997); program(s) used to refine structure: $SHELXL97$ (Sheldrick, 1997); molecular graphics: $SHELXL97$; software used to prepare material for publication: $SHELXL97$.

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