DALTON
FULL PAPER

Acetylacetonatodifluorooxometalates of vanadium and molybdenum: syntheses and crystal structures

Andreas Stasch, Mark Schormann, Jörg Prust, Herbert W. Roesky,* Hans-Georg Schmidt and Mathias Noltemeyer

Institut für Anorganische Chemie der Georg-August-Universität Göttingen, Tammannstr. 4, 37077 Göttingen, Germany. E-mail: hroesky@gwdg.de

Received 22nd January 2001, Accepted 15th May 2001
First published as an Advance Article on the web 12th June 2001

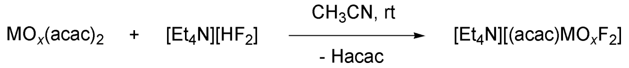
$[Et_4N][HF_2]$ reacted with $VO(acac)_2$ and $MoO_2(acac)_2$ in acetonitrile at room temperature with elimination of Hacac to produce the metalates $[Et_4N][(acac)VOF_2]$ **1** and $[Et_4N][(acac)MoO_2F_2]$ **2**, respectively. These compounds are the first examples of fluorometalates of vanadium and molybdenum bearing the acetylacetonato group. The crystal structures have been determined.

Introduction

There is considerable interest in preparing new materials with catalytic activity. Vanadium compounds *e.g.* $VO(acac)_2$ have been used to prepare a large number of catalysts, mainly for oxidation reactions.[1] Furthermore, some vanadium(IV) compounds serve as insulin-mimetic agents.[2] Fluoride ions in metal fluorides act as structure directing and mineralising agents[3] and alkyl ammonium cations show a template effect in sol–gel systems.[4] $[n\text{-}Bu_4N][HF_2]$ reacts with silanes,[5] Group 13 trialkylmetalanes,[6] titanium isopropoxide and an organoalumophosphonate[7] to form fluorometalates. Our interest is focused on the syntheses of fluorometalates that combine the solubility properties of the acac ligand and the properties of the metal–fluorine units.

Results and discussion

Treatment of $VO(acac)_2$ and $MoO_2(acac)_2$ with $[Et_4N][HF_2]$[8] in acetonitrile at room temperature yielded the metalates $[Et_4N][(acac)VOF_2]$ **1** and $[Et_4N][(acac)MoO_2F_2]$ **2**, respectively, in good yields (Scheme 1). In this reaction the hydrogen difluoride ion eliminates an Hacac ligand by protonolyses and two fluoride ions are transferred to the metal centre. Compound **1** crystallises in the orthorhombic space group *Pbca*. The crystal structure is depicted in Fig. 1. The anion of **1** consists of a six-membered ring bearing vanadium and the acac ligand (O(1)C(2)C(3)C(4)O(2)) and two fluorine and one oxygen atom bonded to the distorted trigonal bipyramidal coordinated metal centre. The average V–F distance is 187.2 pm and the F–V–F angle 87.60(7)°. A selection of bond lengths and angles is shown in Table 1. Compound **2** crystallises in the monoclinic space group *Cc*. The crystal structure is depicted in Fig. 2. The structure is homologous to that of **1** with the exception of an additional oxygen atom at the metal centre. The molybdenum atom is in a distorted octahedral coordination sphere. The average Mo–F bond length is 191.2 pm and the F–Mo–F angle was determined to be 157.24(15)°. A selection of bond lengths and angles is given in Table 2.



$$MO_x(acac)_2 + [Et_4N][HF_2] \xrightarrow[\text{- Hacac}]{CH_3CN,\ rt} [Et_4N][(acac)MO_xF_2]$$

Scheme 1 **1**: M = V, x = 1; **2**: M = Mo, x = 2.

Table 1 Selected bond lengths (pm) and angles (°) for **1**

V(1)–F(1)	187.4(2)	V(1)–F(2)	187.0(2)
V(1)–O(1)	200.3(2)	V(1)–O(2)	201.0(2)
V(1)–O(3)	159.5(2)	O(1)–C(2)	127.8(3)
O(2)–C(4)	127.5(3)	C(1)–C(2)	150.2(4)
C(2)–C(3)	138.6(4)	C(3)–C(4)	139.4(4)
C(4)–C(5)	150.1(4)		
F(2)–V(1)–F(1)	87.60(7)	F(1)–V(1)–O(1)	84.74(7)
F(1)–V(1)–O(2)	150.00(8)	F(2)–V(1)–O(1)	148.05(8)
O(3)–V(1)–F(2)	108.61(9)	O(3)–V(1)–F(1)	106.93(9)
F(2)–V(1)–O(2)	84.72(7)	O(1)–V(1)–O(2)	86.60(8)
O(3)–V(1)–O(1)	103.30(9)	O(3)–V(1)–O(2)	103.00(8)
C(2)–O(1)–V(1)	130.0(2)	C(4)–O(2)–V(1)	129.9(2)
O(1)–C(2)–C(3)	124.8(3)	O(1)–C(2)–C(1)	115.6(3)
C(3)–C(2)–C(1)	119.6(3)	C(2)–C(3)–C(4)	123.9(3)
O(2)–C(4)–C(3)	124.7(3)	O(2)–C(4)–C(5)	115.7(3)
C(3)–C(4)–C(5)	119.6(3)		

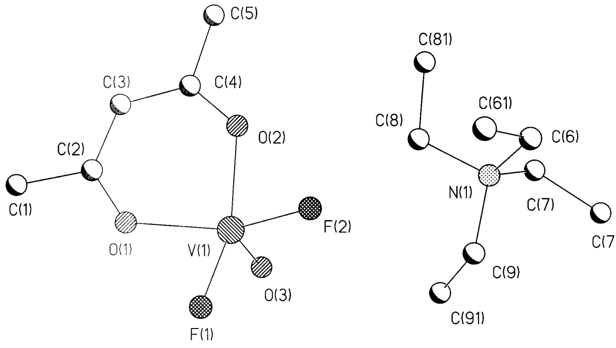


Fig. 1 Molecular structure of **1**.

The NMR spectra of **1** and **2** are consistent with the solid state structures. The NMR resonances of **1** are broad due to the paramagnetic properties of the vanadium(IV) ion. The ^{19}F NMR resonances of **1** and **2** are singlets at −124.6 and −53.0 ppm, respectively, referred to $CFCl_3$. In the ^{51}V NMR spectrum of **1** a resonance (−588.3 ppm) with unclear multiplicity is observed while the ^{95}Mo NMR spectrum of **2** shows a sharp triplet (J = 114 Hz) at −73.6 ppm. The ESR spectrum of **1** in solution at room temperature shows an octet at 324 mT due to coupling ($|a_V|$ = 11 mT) of an unpaired electron with the $^{51}V(IV)$ (I = 7/2) nucleus and is depicted in Fig. 3. FAB ion mass

DOI: 10.1039/b100740h

This journal is © The Royal Society of Chemistry 2001

Table 2 Selected bond lengths (pm) and angles (°) for **2**

Mo(1)–F(1)	192.9(6)	Mo(1)–F(2)	190.4(6)
Mo(1)–O(1)	218.2(8)	Mo(1)–O(2)	216.2(8)
Mo(1)–O(3)	171.4(10)	Mo(1)–O(4)	167.8(10)
O(1)–C(1)	130.1(18)	C(1)–C(2)	140(2)
C(1)–C(5)	151.2(15)	O(2)–C(3)	124.5(16)
C(2)–C(3)	140(2)	C(3)–C(4)	149.3(16)
F(1)–Mo(1)–F(2)	157.24(15)	F(1)–Mo(1)–O(1)	79.9(3)
F(1)–Mo(1)–O(2)	80.7(3)	F(1)–Mo(1)–O(3)	95.7(4)
F(1)–Mo(1)–O(4)	98.0(4)	F(2)–Mo(1)–O(1)	81.9(3)
F(2)–Mo(1)–O(2)	82.6(3)	F(2)–Mo(1)–O(3)	96.3(4)
F(2)–Mo(1)–O(4)	97.8(4)	O(1)–Mo(1)–O(2)	79.33(12)
O(1)–Mo(1)–O(3)	85.2(4)	O(1)–Mo(1)–O(4)	170.8(4)
O(2)–Mo(1)–O(3)	164.5(4)	O(2)–Mo(1)–O(4)	91.5(4)
O(3)–Mo(1)–O(4)	103.9(2)	C(1)–O(1)–Mo(1)	132.1(8)
C(3)–O(2)–Mo(1)	134.9(8)	O(1)–C(1)–C(2)	124.6(11)
C(2)–C(1)–C(5)	120.5(11)	O(1)–C(1)–C(5)	114.9(11)
O(2)–C(3)–C(2)	124.8(11)	C(3)–C(2)–C(1)	124.1(4)
C(2)–C(3)–C(4)	119.1(12)	O(2)–C(3)–C(4)	116.0(11)

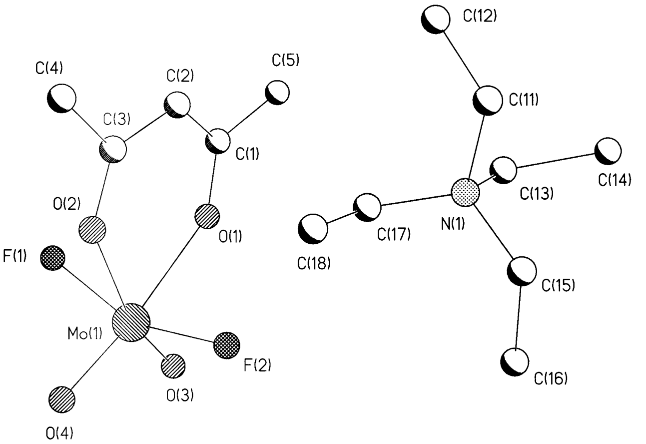


Fig. 2 Molecular structure of **2**.

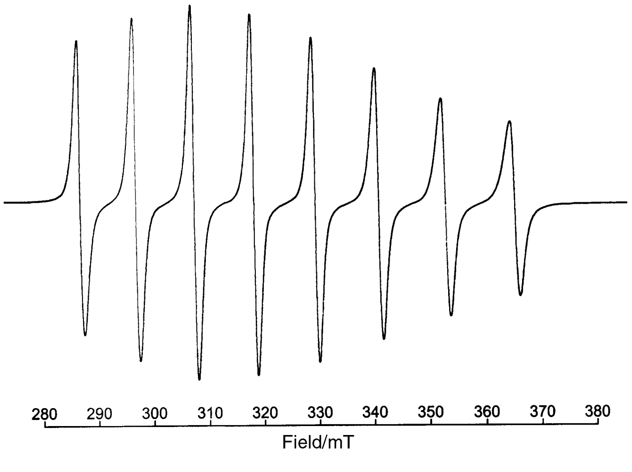


Fig. 3 ESR spectrum of **1** in solution at 295 K.

spectroscopy always gives the value for $[Et_4N]^+$ (130, 100%) as the only dominating ion in the cation accelerated spectrum. For **1** the fragment for M + $[Et_4N]$ (464, 3%) can also be observed. Consequently, the FAB anion accelerated spectrum of **1** shows the anion (204, 100%) and M + $[(acac)VOF_2]$ (538, 4%) while for **2** the anion plus 31 (298, 100%) is observed in the correct isotope pattern along with numerous signals of the matrix (3-nitrobenzyl alcohol). The value of 31 might be due to a CH_3O group transferred from the matrix to the anion. The IR metal fluorine stretching frequencies of **1** (520, 486 cm^{-1}) and **2** (570, 549 cm^{-1}) were tentatively assigned.

The homologous compounds to **1** and **2**, $[n\text{-}Bu_4N][(acac)VOF_2]$ and $[n\text{-}Bu_4N][(acac)MoO_2F_2]$, can be obtained as oily crude products from the reaction of $[n\text{-}Bu_4N][HF_2]$ with $VO(acac)_2$ and $MoO_2(acac)_2$, respectively, in common organic solvents.

Conclusion

The reaction of quaternary ammonium hydrogen difluorides with $VO(acac)_2$ and $MoO_2(acac)_2$ provides mixed acetylacetonatodifluorooxometalates which are – to the best of our knowledge – the first fluorometalates of vanadium and molybdenum bearing the acetylacetonato ligand. These compounds are promising precursors for the preparation of new oxide catalysts. Currently, we are working on the preparation of new fluorometalates using hydrogen difluorides.

Experimental

General

All manipulations were performed under a dry and oxygen free nitrogen atmosphere using Schlenk line and glove box techniques. Solvents were dried and distilled prior to use. $VO(acac)_2$ and $MoO_2(acac)_2$ are commercially available and were used as received. $[Et_4N][HF_2]$ was prepared by the literature method.[8] Melting points are not corrected. FAB anion spectra were recorded after treatment with 3-nitrobenzyl alcohol in air.

Preparations

$[Et_4N][(acac)VOF_2]$ 1. A mixture of $VO(acac)_2$ (1.11 g, 4.19 mmol) and $[Et_4N][HF_2]$ (0.71 g, 4.19 mmol) in CH_3CN (15 cm^3) was stirred at room temperature for one day. A small amount of precipitate was filtered off and the solvent was removed under reduced pressure. *n*-Hexane (15 cm^3) and THF (10 cm^3) were added and the crude product was filtered. Recrystallisation from CH_3CN/THF (1 : 1) afforded **1** as green cubes (1.00 g, 72%), mp 190 °C (Found: C, 46.88; H, 8.13; N, 4.35. $C_{13}H_{27}F_2NO_3V$ requires C, 46.71; H, 8.14; N, 4.19%); IR (KBr): $\tilde{\nu}/cm^{-1}$ 2990, 1631, 1563, 1534, 1489, 1442, 1421, 1396, 1360, 1288, 1175, 1025, 997, 974, 952, 790, 687, 659, 610, 520, 486, 425, 367, 343; ^1H NMR (200 MHz, solvent CD_3CN, standard TMS): δ 1.19 [s, br, 12 H, CH_2CH_3], 1.93 [s, br, 6 H, acac-CH_3], 2.62 [s, br, 1 H, acac-H], 3.17 [s, br, 8 H, CH_2CH_3]; ^{19}F NMR (188 MHz, solvent CD_3CN, standard $CFCl_3$): δ −124.6 [s, br]; ^{51}V NMR (65.8 MHz, solvent CD_3CN, standard $VOCl_3$): δ −588.3 [m_c]; ESR (295 K, solution in CD_3CN): 324 mT (^{51}V(IV), octet, $|a_V| = 11$ mT); $m/z_{FAB\ cation}$: 464 (M + $[Et_4N]^+$, 3), 130 ($[Et_4N]^+$, 100), $m/z_{FAB\ anion}$: 538 (M + $[(acac)VOF_2]^-$, 4), 204 ($[(acac)VOF_2]^-$, 100).

$[Et_4N][(acac)MoO_2F_2]$ 2

A suspension of $MoO_2(acac)_2$ (1.04 g, 3.19 mmol) and $[Et_4N][HF_2]$ (0.54 g, 3.19 mmol) in CH_3CN (10 cm^3) was stirred at room temperature for 7 h. The precipitate was filtered off and the solution was stored for 4 days at −25 °C to yield **2** as light-yellow polyhedral crystals (0.98 g, 78%), mp 179 °C, (Found: C, 39.63; H, 6.96; N, 3.67. $C_{13}H_{27}F_2NMoO_4$ requires C, 39.50; H, 6.88; N 3.54%); IR (KBr): $\tilde{\nu}/cm^{-1}$ 2987, 2960, 2922, 1591, 1525, 1485, 1444, 1378, 1274, 1195, 1174, 1028, 1003, 936, 898, 816, 786, 662, 570, 549, 416, 383; ^1H NMR (200 MHz, solvent CD_3CN, standard TMS): δ 1.20 [tt, $J = 7.3$ Hz, $J = 1.9$ Hz, 12 H, CH_2CH_3], 1.91 [s, 6 H, acac-CH_3], 3.16 [q, $J = 7.3$ Hz, 8 H, CH_2CH_3], 5.53 [s, 1 H, acac-H]; ^{19}F NMR (188 MHz, solvent CD_3CN, standard $CFCl_3$): δ −53.0 [s]; ^{95}Mo NMR (32.6 MHz, solvent CD_3CN, standard Na_2MoO_4): δ −73.6 [t, $J = 114$ Hz]; $m/z_{FAB\ cation}$: 130 ($[Et_4N]^+$, 100), $m/z_{FAB\ anion}$: 298 ($[(acac)MoO_2F_2]^-$ + CH_3O, 100).

Table 3 Crystallographic data for **1** and **2**

	1	**2**
Molecular formula	$C_{13}H_{27}F_2NO_3V$	$C_{13}H_{27}F_2MoNO_4$
M	334.30	395.30
T/K	200(2)	200(2)
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*Cc*
a/pm	1306.0(2)	1571.8(3)
b/pm	1260.46(11)	816.49(10)
c/pm	2046.7(4)	1342.1(3)
α/°	90	90
β/°	90	98.644(15)
γ/°	90	90
U/nm^3	3.3692(9)	1.7029(5)
Z	8	4
D/Mg m^{-3}	1.318	1.542
μ/mm^{-1}	0.614	0.803
F(000)	1416	816
Reflections collected/unique	3277/2976	2381/2377
R_{int}	0.0238	0.0451
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0402, 0.0933	0.0414, 0.1082
(all data)	0.0586, 0.1198	0.0416, 0.1086

X-Ray crystallography

The data were collected on a Stoe Siemens four circle diffractometer with $Mo_{K\alpha}$-radiation on rapidly cooled crystals suspended in oil with profile optimised $2\theta/\omega$-scans. The structure was solved using direct methods (SHELXS-97) and was refined by full matrix least squares on F^2 (SHELXL-97).[9] Crystallographic data are summarized in Table 3.

CCDC reference numbers 154686 and 154687.

See http://www.rsc.org/suppdata/dt/b1/b100740h/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for financial support.

References

1 P. J. Gellings, *Catalysis*, 1985, **7**, 105; I. E. Wachs, *Catalysis*, 1997, **13**, 37; P. Van Der Voort, K. Possemiers and E. F. Vansant, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 843; U. Klett and J. Fricke, *J. Non-Cryst. Solids*, 1998, **225**, 188; M. Baltes, P. Van Der Voort, O. Collart and E. F. Vansant, *J. Porous Mater.*, 1998, **5**, 317; S. Y. Yu, T. Hayakawa and M. Ueda, *Chem. Lett.*, 1999, 559; Y. Taniguchi, T. Hayashida, H. Shibasaki, D. G. Piao, T. Kitamura, T. Yamaji and Y. Fujiwara, *Org. Lett.*, 1999, **1**, 557; D. R. Pesiri, D. K. Morita, T. Walker and W. Tumas, *Organometallics*, 1999, **18**, 4916; M. Baltes, P. Van Der Voort, B. M. Weckhuysen, R. R. Rao, G. Catana, R. A. Schoonheydt and E. F. Vansant, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2673.

2 A. S. Tracy and D. C. Crans, *Vanadium Compounds – Chemistry, Biochemistry, and Therapeutic Applications*, American Chemical Society, Washington, DC, 1998.

3 H. W. Roesky and I. Haiduc, *J. Chem. Soc., Dalton Trans.*, 1999, 2249; H. W. Roesky, *Inorg. Chem.*, 1999, **38**, 5934.

4 T. Fujita, T. Yamaguchi, S. Taruta and K. Kitajima, *J. Ceram. Soc. Jpn.*, 1999, **107**, 353; J. El Haskouri, M. Roca, S. Cabrera, J. Alamo, A. Beltran-Porter, D. Beltran-Porter, M. D. Marcos and P. Amoros, *Chem. Mater.*, 1999, **11**, 1446; D. J. Abdallah and R. G. Weiss, *Chem. Mater.*, 2000, **12**, 406; G. B. Saupe, C. C. Waraksa, H. N. Kim, Y. J. Han, D. M. Kaschak, D. M. Skinner and T. E. Mallouk, *Chem. Mater.*, 2000, **12**, 1556.

5 D. Albanese, D. Landini and M. Penso, *Tetrahedron Lett.*, 1995, **36**, 8865.

6 H. W. Roesky, A. Stasch, H. Hatop, C. Rennekamp, D. H. Hamilton, M. Noltemeyer and H.-G. Schmidt, *Angew. Chem.*, 2000, **112**, 177; *Angew. Chem., Int. Ed.*, 2000, **39**, 171.

7 D. Chakraborty, S. Horchler, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Inorg. Chem.*, 2000, **39**, 3995.

8 F. Y. Fujiwara and J. S. Martin, *J. Am. Chem. Soc.*, 1974, **96**, 7625.

9 G. M. Sheldrick, SHELX-97, program for crystal structure refinement, Universität Göttingen, 1997.