Homoleptic Vanadium(III) Diacetone Glucosides: how to make a Lewis Acid Chiral. Crystal Structure of Tris-(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranosato- κO^3)-bis(pyridine)vanadium(III)†

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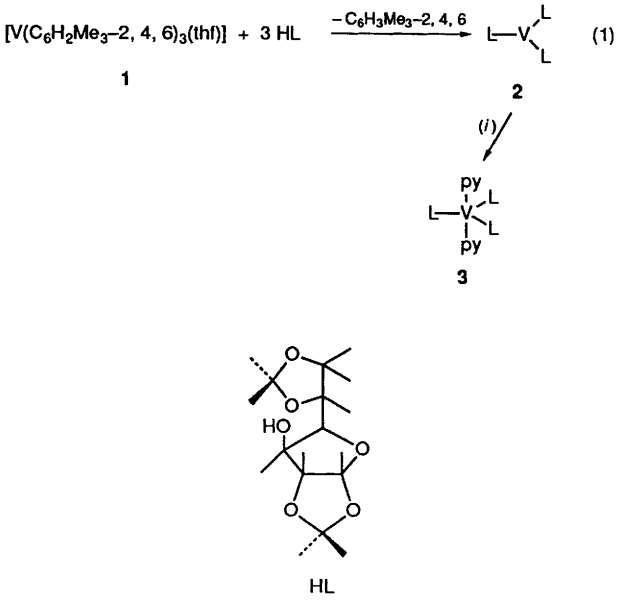
The synthesis of the first homoleptic glucose derivative of a transition metal was achieved *via* the protonolysis of $[V(C_6H_2Me_3\text{-}2,4,6)_3(thf)]$ (thf = tetrahydrofuran) using the monoprotic ligand 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (HL). The complex $[VL_3]$ was converted by addition of pyridine (py) into $[VL_3(py)_2]$ containing a metal chiral centre as shown by X-ray analysis.

Metal-carbohydrate derivatives with the metal covalently bonded to the carbohydrate skeleton are fairly exotic species.[1] Sugars or protected sugars should be considered like an alkoxo or polyalkoxo skeleton with some very interesting features. Their unique use as ancillary ligands in combination with the cyclopentadienyl ligand has recently been reported,[2] while there is no example of any homoleptic derivative containing as sole ligand a sugar residue. The diversified interest in this field comes from different areas: (*i*) the asymmetric induction caused by organometallic complexes containing chiral ligands;[3] (*ii*) the synthesis of chiral Lewis acids or bases;[3] (*iii*) a significant novel version of metal–alkoxo chemistry;[4] and (*iv*) the potential use of oxygen-rich complexes as ligands in metal aggregates.[4]

Results and Discussion

The present report deals with an easy and general synthesis of the metal–glucose functionality of early transition metals. The reaction consists of treating the aryl derivative of vanadium(III), $[V(C_6H_2Me_3\text{-}2,4,6)_3(thf)]$ (thf = tetrahydrofuran), with the monoprotic ligand 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (HL) as exemplifed in reaction (1) of Scheme 1.

The starting alkyl **1**[5] is an easily accessible material. Reaction (1) has been carried out at room temperature in toluene, and the yield is 93%. Complex **2** was isolated as a pink crystalline solid, monomeric in benzene. Since **2** may not be obtained in a crystalline form suitable for an X-ray analysis, it was recrystallized in the presence of pyridine and obtained in the form of $[VL_3(py)_2]$ **3**. The structure of **3** was determined by an X-ray analysis and is discussed below.



Scheme 1 (*i*) Pyridine (py), toluene

Vanadium(III) binds three oxygen atoms from the sugar residues in the equatorial plane of a trigonal bipyramid, which is completed by two axial pyridines, omitted for clarity in Fig. 1. The V–O distances [average 1.850(5) Å] indicate a multiple bond and are at the lower limit of those found in the aryl-oxovanadium(III) derivatives.[6] The vanadium atom deviates by 0.043(1) Å from the equatorial plane, C(4) and C(4″) are out of that plane on the same side as vanadium, while C(4′) is located on the opposite side. The molecule belongs to a chiral space group and the structure corresponds to the absolute configuration, which is unequivocally determined by the X-ray analysis. Such an attribution allows us to draw some conclusions.

(*i*) The sugar molecules have the same D configuration, being related to each other by simple rotation.

(*ii*) Complex **3** shows a left-handed (Λ)‡ helical chirality, so

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xxviii–xxii.

‡ The arrangement of the chiral ligands around the metal centre gives rise to two possible enantiomers Λ or Δ corresponding to a clockwise or anticlockwise arrangement of the molecule. According to this assignment, we have designated **3** as the Λ enantiomer.

Table 1 Fractional atomic coordinates (10^4) for complex **3**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
V	−1687(1)	0(−)	−2558(1)
O(1)	−5077(8)	−1990(5)	−525(6)
O(2)	−5081(6)	−987(3)	−1431(4)
O(3)	−4180(5)	−1933(3)	−3585(4)
O(4)	−2942(4)	−642(3)	−3023(4)
O(5)	−5523(6)	−828(3)	−5237(4)
O(6)	−5129(6)	−1979(4)	−5368(5)
C(1)	−4861(9)	−2174(5)	−1557(7)
C(2)	−4410(7)	−1492(4)	−1919(6)
C(3)	−4740(6)	−1372(4)	−3096(5)
C(4)	−4216(6)	−719(4)	−3500(5)
C(5)	−4273(7)	−910(5)	−4640(6)
C(6)	−4127(7)	−1711(5)	−4599(7)
C(7)	−5388(9)	−1287(6)	−515(7)
C(8)	−4603(13)	−964(8)	454(8)
C(9)	−6770(13)	−1208(9)	−516(13)
C(10)	−5814(8)	−1409(6)	−5923(6)
C(11)	−7203(9)	−1609(6)	−6059(8)
C(12)	−5423(16)	−1322(9)	−6955(9)
O(1′)	1949(8)	2107(5)	−4740(8)
O(2′)	1519(6)	1094(4)	−4001(6)
O(3′)	−1561(5)	1891(3)	−4830(4)
O(4′)	−1419(5)	677(3)	−3498(4)
O(5′)	−2571(5)	632(3)	−6305(4)
O(6′)	−3077(6)	1769(3)	−6365(4)
C(1′)	1095(10)	2253(5)	−4136(9)
C(2′)	535(9)	1550(5)	−3947(7)
C(3′)	−627(7)	1351(4)	−4779(5)
C(4′)	−1275(7)	702(4)	−4542(5)
C(5′)	−2581(7)	813(4)	−5250(6)
C(6′)	−2733(7)	1605(4)	−5281(6)
C(7′)	2495(10)	1465(8)	−4384(13)
C(8′)	2710(15)	1093(11)	−5352(17)
C(9′)	3620(12)	1512(10)	−3567(15)
C(10′)	−3232(9)	1170(5)	−6973(7)
C(11′)	−4604(13)	952(7)	−7311(15)
C(12′)	−2663(15)	1262(9)	−7909(9)
O(1″)	2427(14)	1637(7)	611(10)
O(2″)	750(7)	1381(4)	−582(6)
O(3″)	1198(5)	−289(3)	760(5)
O(4″)	−687(4)	−102(3)	−1220(3)
O(5″)	−1282(5)	−254(3)	1417(4)
O(6″)	338(7)	−1015(4)	1879(4)
C(1″)	2641(11)	942(9)	455(14)
C(2″)	1344(7)	739(5)	−240(8)
C(3″)	595(7)	361(4)	403(6)
C(4″)	−721(6)	126(4)	−196(5)
C(5″)	−969(7)	−482(4)	460(5)
C(6″)	326(10)	−813(5)	833(6)
C(7″)	1452(19)	1949(8)	−35(11)
C(8″)	1747(16)	2451(9)	−835(15)
C(9″)	644(32)	2318(11)	674(20)
C(10″)	−491(11)	−594(5)	2297(7)
C(11″)	215(10)	−34(7)	3043(7)
C(12″)	−1296(16)	−1020(7)	2837(10)
N(21)	−2857(5)	740(3)	−1965(4)
C(22)	−3717(7)	545(5)	−1436(6)
C(23)	−4285(8)	1022(7)	−893(7)
C(24)	−3984(12)	1719(7)	−906(8)
C(25)	−3147(12)	1916(5)	−1449(9)
C(26)	−2603(9)	1433(5)	−1982(7)
N(31)	−400(5)	−728(3)	−3067(4)
C(32)	709(7)	−512(5)	−3233(6)
C(33)	1602(9)	−950(6)	−3460(9)
C(34)	1370(9)	−1658(6)	−3503(8)
C(35)	210(11)	−1881(5)	−3314(9)
C(36)	−641(8)	−1415(4)	−3107(7)

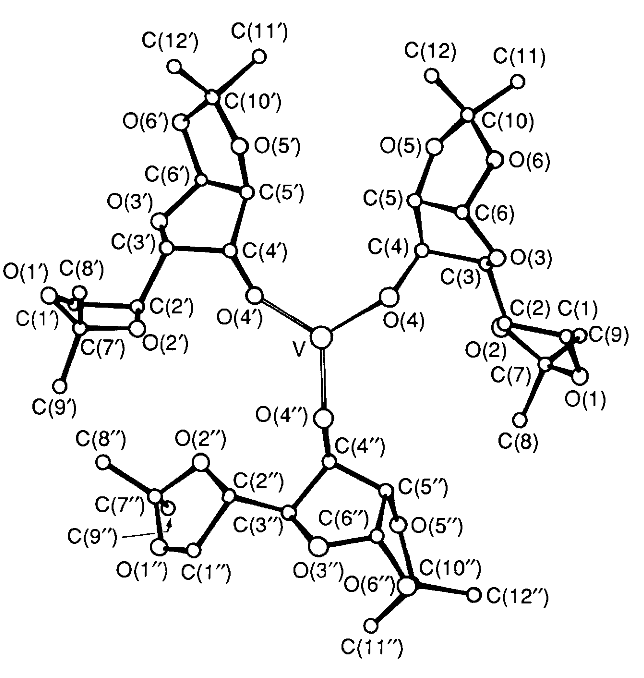

Fig. 1 A view of complex **3** perpendicular to the VO_3 plane [pyridine rings, bonded *trans* to each other through N(21) and N(31), are omitted for clarity]. Bond distances (Å): V–O(4) 1.852(5), V–O(4′) 1.848(5), V–O(4″) 1.851(5), V–N(21) 2.161(6) and V–N(31) 2.183(6). Bond angles (°): N(21)–V–N(31) 176.1(2), O(4)–V–O(4′) 118.0(2), O(4)–V–O(4″) 119.0(2), O(4′)–V–O(4″) 123.0(2), V–O(4)–C(4) 144.1(5), V–O(4′)–C(4′) 136.6(5) and V–O(4″)–C(4″) 136.1(4)

we found only one of the two Λ, Δ enantiomers possible on the basis of the D-sugar chirality.

(*iii*) The Λ configuration allows two conformers, the most asymmetric one being present in our structure. The second one, having an approximate C_3 symmetry, can be generated by a simple rotation of 180° around the V–O(4′) bond. Such a rotation, however, is energetically forbidden. A calculation of the potential energy as a function of the torsional angle around the V–O(4′) vector was carried out.[7] Considering the target molecule, including the hydrogen atoms, and making a rotation of 360° around V–O(4′), we found two minima in the ranges 320–100 and 170–220° and two potential-energy barriers having maxima at *ca.* 130 and 180°. Therefore, the two conformers of the Λ configuration are not interconvertible by simple rotation.

The two axial pyridines do not affect the chirality of the metal centre. The monomeric nature of **2** in benzene is quite remarkable. The VO_3 fragment does not seem to suffer much for its unsaturation unless we admit the intramolecular intervention of the oxygens from the sugar ligands. This, however, seems rather unlikely because of the rigidity of the ligand, and the wide V–O–C angles observed in the related complex **3**. Such angle values, in addition to the short V–O distances, support multiple bonding between the oxygen atoms and vanadium.[4] This fact should be taken into consideration of the unusual stability of the three-co-ordination in **2**. Complex **2** shows its Lewis acidity in binding the axial pyridines.

A special focus will be placed on the chemistry of metals in such unusual co-ordination environments, including their use in asymmetric synthesis.

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Magnetic moments were determined with a Faraday balance. The complex $[V(C_6H_2Me_3\text{-}2,4,6)_3(thf)]$ **1** was prepared as reported.[5]

Preparations.—$[VL_3]$ **2**. The solid ligand HL (8.25 g, 31.6 mmol) was added to a toluene (80 cm^3) suspension of complex **1** (4.97 g, 10.36 mmol). The resulting pink solution formed in a few minutes was evaporated to 30 cm^3. By addition of hexane (30 cm^3), pink-violet crystals of $[VL_3]$ **2** were obtained on standing at room temperature for 12 h, yield 93% [Found: C, 52.40; H, 6.95; V, 6.20%; *M* (cryoscopy in benzene) 832. $C_{36}H_{57}O_{18}V$ requires C, 52.15; H, 6.95; V, 6.15%; *M* 828]. μ_{eff} 2.59 at 288 K, α(thf, 0.117 mol dm^{-3}, 297 K, 546 nm) = −200.7°.

$[VL_3(py)_2]$ **3**. Pyridine (0.30 cm^3, 3.70 mmol) was added to a toluene (50 cm^3) solution of complex **2** (1.43 g, 1.73 mmol). The resulting orange solution was evaporated to dryness and the residue, recrystallized from hexane, gave orange crystals of **3** (60%) (Found: C, 56.05; H, 6.65; N, 2.80. $C_{46}H_{67}N_2O_{18}V$ requires C, 56.00; H, 6.85; N, 2.85%). μ_{eff} 2.77 at 295 K, α(thf, 0.073 mol dm^{-3}, 297 K, 546 nm) = −226°.

Crystal Structure Determination.—Crystals of complex **3** were sealed in capillaries under nitrogen because of their high sensitivity to moisture.

Crystal data. $C_{46}H_{67}N_2O_{18}V$, $M = 987.0$, monoclinic, space group $P2_1$, $a = 10.912(1)$, $b = 19.310(2)$, $c = 12.912(1)$ Å, $\beta = 102.05(1)°$, $U = 2660.8(4)$ Å^3, $Z = 2$, $D_c = 1.232$ g cm^{-3}, Cu-Kα radiation ($\lambda = 1.5418$ Å), μ(Cu-Kα) = 21.31 cm^{-1}. Crystal dimensions 0.38 × 0.46 × 0.55 mm.

The structure was solved by the heavy-atom method (Patterson and Fourier synthesis) and refined by full-matrix least squares. For 3270 unique observed structure amplitudes $[I > 2\sigma(I)]$, corrected for absorption, collected at room temperature on a Siemens AED diffractometer in the range $6 < 2\theta < 140$, the *R* value was 0.061 ($R_G = 0.066$); $R = 0.076$ and $R_G = 0.081$ for the incorrect enantiomorph. The absolute configuration was established and the final coordinates correspond to the correct enantiomorph. All the hydrogen atoms were put in geometrically calculated positions and introduced as fixed contributors in the final stage of refinement. All calculations were carried out using SHELX 76.[8] Atomic coordinates for complex **3** are listed in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 20-28470.90) and Ciba-Geigy Company (Basel) for financial support.

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Received 21*st February* 1991; *Paper* 1/00824B