Crystal structure of (1,10-phenanthroline- κ^2N,N')oxo(*N*-salicylidene-isoleucinato- κ^3O,N,O')vanadium(IV), VO(C₁₂H₈N₂)(C₁₃H₁₅NO₃)

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Abstract

C₂₅H₂₃N₃O₄V, trigonal, $R\bar{3}$ (no. 148), $a = 32.59(1)$ Å, $c = 10.974(4)$ Å, $V = 10096$ Å³, $Z = 18$, $R_{\text{gt}}(F) = 0.053$, $wR_{\text{ref}}(F^2) = 0.152$, $T = 293$ K.

Source of material

Salicylaldehyde (2 mmol, 0.21 ml) was dissolved in hot ethanol (10 ml) and was added slowly to the mixture of D,L-isoleucine (2 mmol, 262.4 mg) and potassium hydroxide (2 mmol, 112 mg). After stirring for 1 h, this mixture was added successively to the solution of vanadyl sulfate hydrate (2 mmol, 451 mg) in 4 ml water and further refluxed for 4 h. Subsequently, ethanol solution of 1,10-phenanthroline monohydrate (2 mmol, 396 mg) was dropped gradually into the reaction mixture and refluxed for 3 h, obtaining a deep yellow solution. It was filtered and held at room temperature for seven days, whereupon yellow crystals suitable for X-ray diffraction were obtained.

Discussion

Vanadium is a biologically essential trace element, encountered in metalloenzymes such as haloperoxidases or nitrogenases. Since vanadyl cation has been tested as a component of oral insulin-mimetic substances in humans [1], the coordination chemistry of oxovanadium(IV) (i.e. VO²⁺ or vanadyl) is currently of great interest. But compared with other transition metal complexes, less vanadium complexes have been synthesized and characterized. In the course of studying oxovanadium(IV) complexes [2,3], a V(IV) complex with 1,10-phenanthroline and a tridentate Schiff base ligand derived from salicylaldehyde and D,L-isoleucine was synthesized and its crystal structure determined.

In the title complex, the central vanadium(IV) atom is in a distorted octahedral environment with six ligand atoms. The terminal oxo O4 and the N3 atom from 1, 10-phenanthroline occupy the axial positions with an O4–V1–N3 angle of 167.6(2)°. The N2 atom from the phenanthroline and the N1, O1 and O3 atoms from the tridentate Schiff base form the equatorial plane of the coordination polyhedron. The V^{IV} atom is displaced towards the O4 by 0.291(2) Å from the equatorial plane. The V=O distance of 1.585(3) Å is very close to that value reported for another six-coordinated Schiff base oxovanadium(IV) complex, [V(C₁₇H₁₅NO₅)O(C₁₀H₈N₂)] · CH₃OH · H₂O [2], which is characteristic for oxovanadium(IV) complexes (1.588 Å – 1.601 Å) [1]. The V1–O1 and the V1–O3 bond distances, 1.980(3) Å and 1.921(3) Å, respectively, are in the range observed for many vanadium Schiff base complexes [1,3–5] and due to the Jahn–Teller effect. The Schiff base forms two chelating rings to the vanadium atom, O1, C1, C2, N1, V1 and N1, C7–C9, O3, V1, which have the dihedral angle 12.3(2)° and 7.5(2)° to the equatorial plane, respectively. The least-squares plane of 1,10-phenanthroline ligand is almost perpendicular to the equatorial plane (dihedral angle 88.47(7)°). In the molecule, pairs of 1,10-phenanthroline ligands related by the symmetry center have ring centroid-centroid separations of 3.42 Å and 3.45 Å (perpendicular distance 3.58 Å) for the N2, C14–C18 and C17–C20, C24, C25 rings, respectively, indicating significant π - π interactions [6].

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.06 × 0.28 × 0.32 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	4.80 cm ⁻¹
Diffractionmeter, scan mode:	Bruker SMART CCD, ϕ/ω
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	17804, 3950
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1713
$N(\text{param})_{\text{refined}}$:	309
Programs:	SHELXS-97 [7], SHELXL-97 [8]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U _{iso}
H(2)	18f		0.0275	0.1307	0.0989	0.071
H(3)	18f	0.54	0.0725	0.0964	0.1505	0.099
H(3')	18f	0.46	0.0455	0.1052	0.2776	0.099
H(4A)	18f		0.1132	0.1627	0.3337	0.129
H(4B)	18f		0.1389	0.1598	0.2163	0.129
H(5A)	18f		0.1057	0.0914	0.4043	0.250
H(5B)	18f		0.1592	0.1278	0.3789	0.250
H(5C)	18f		0.1299	0.0871	0.2853	0.250
H(6A)	18f	0.54	0.0009	0.0666	0.2488	0.211
H(6B)	18f	0.54	0.0265	0.0998	0.3601	0.211
H(6C)	18f	0.54	0.0377	0.0598	0.3252	0.211
H(6A')	18f	0.46	0.0259	0.0592	0.1066	0.245
H(6B')	18f	0.46	0.0573	0.0491	0.1963	0.245
H(6C')	18f	0.46	0.0798	0.0793	0.0785	0.245

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U _{iso}
H(7)	18f		-0.0030	0.1423	0.2838	0.064
H(10)	18f		0.0366	0.3153	0.3948	0.083
H(11)	18f		-0.0272	0.2806	0.5202	0.091
H(12)	18f		-0.0650	0.2002	0.5583	0.090
H(13)	18f		-0.0441	0.1542	0.4468	0.081
H(14)	18f		0.2055	0.3464	0.2001	0.069
H(15)	18f		0.2521	0.4159	0.0972	0.077
H(16)	18f		0.2247	0.4333	-0.0736	0.076
H(21)	18f		0.0074	0.2772	-0.2531	0.077
H(22)	18f		-0.0323	0.2081	-0.1448	0.074
H(23)	18f		0.0036	0.1966	0.0232	0.068
H(24)	18f		0.1555	0.4110	-0.2175	0.079
H(25)	18f		0.0814	0.3578	-0.2794	0.083

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
V(1)	18f		0.10850(3)	0.25443(3)	0.18071(7)	0.0474(6)	0.0526(6)	0.0441(5)	0.0236(5)	0.0021(4)	0.0045(4)
N(1)	18f		0.0554(1)	0.1865(1)	0.2112(4)	0.042(3)	0.051(3)	0.058(3)	0.023(2)	0.005(2)	0.004(2)
N(2)	18f		0.1499(1)	0.3207(1)	0.0933(3)	0.044(3)	0.049(3)	0.043(2)	0.022(2)	0.001(2)	0.000(2)
N(3)	18f		0.0631(1)	0.2567(1)	0.0161(3)	0.042(3)	0.048(3)	0.045(2)	0.020(2)	0.001(2)	0.000(2)
O(1)	18f		0.1223(1)	0.2200(1)	0.0534(3)	0.054(2)	0.055(2)	0.062(2)	0.026(2)	0.011(2)	0.005(2)
O(2)	18f		0.0986(1)	0.1528(1)	-0.0450(4)	0.099(3)	0.089(3)	0.076(3)	0.056(3)	0.002(2)	-0.019(2)
O(3)	18f		0.0725(1)	0.2780(1)	0.2632(3)	0.065(2)	0.057(2)	0.052(2)	0.031(2)	0.020(2)	0.010(2)
O(4)	18f		0.1479(1)	0.2630(1)	0.2782(3)	0.066(2)	0.071(2)	0.061(2)	0.029(2)	-0.017(2)	0.007(2)
C(1)	18f		0.0950(2)	0.1753(2)	0.0407(5)	0.056(4)	0.068(4)	0.062(4)	0.036(3)	-0.005(3)	-0.010(3)
C(2)	18f		0.0582(2)	0.1499(2)	0.1392(5)	0.048(3)	0.051(3)	0.078(4)	0.025(3)	0.000(3)	-0.001(3)
C(3)	18f		0.0689(2)	0.1163(2)	0.2116(6)	0.084(5)	0.073(5)	0.095(5)	0.042(4)	0.008(4)	0.017(4)
C(4)	18f		0.1144(3)	0.1410(2)	0.2752(6)	0.121(6)	0.105(6)	0.105(6)	0.063(5)	-0.022(5)	0.019(5)
C(5)	18f		0.1286(3)	0.1088(3)	0.3422(9)	0.173(9)	0.148(8)	0.21(1)	0.104(7)	-0.064(8)	-0.005(7)
C(6)	18f	0.54(1)	0.0300(5)	0.0826(4)	0.294(2)	0.11(1)	0.10(1)	0.23(2)	0.062(9)	0.08(1)	0.10(1)
C(6')	18f	0.46	0.0569(7)	0.0719(6)	0.142(2)	0.25(3)	0.11(2)	0.19(2)	0.13(2)	0.06(2)	0.02(1)
C(7)	18f		0.0193(2)	0.1745(2)	0.2802(5)	0.045(3)	0.050(3)	0.059(3)	0.020(3)	-0.002(3)	0.013(3)
C(8)	18f		0.0097(2)	0.2055(2)	0.3523(4)	0.040(3)	0.062(4)	0.043(3)	0.024(3)	0.000(3)	0.007(3)
C(9)	18f		0.0359(2)	0.2562(2)	0.3367(4)	0.062(4)	0.070(4)	0.038(3)	0.042(3)	-0.002(3)	0.002(3)
C(10)	18f		0.0205(2)	0.2825(2)	0.4034(5)	0.089(5)	0.083(4)	0.051(3)	0.054(4)	0.007(3)	0.001(3)
C(11)	18f		-0.0172(2)	0.2619(3)	0.4807(5)	0.080(5)	0.121(6)	0.047(4)	0.067(5)	0.010(3)	-0.003(4)
C(12)	18f		-0.0407(2)	0.2139(3)	0.5012(5)	0.059(4)	0.119(6)	0.045(4)	0.042(4)	0.013(3)	0.011(4)
C(13)	18f		-0.0274(2)	0.1868(2)	0.4353(5)	0.052(4)	0.090(4)	0.056(4)	0.033(3)	0.012(3)	0.013(3)
C(14)	18f		0.1936(2)	0.3527(2)	0.1301(5)	0.053(4)	0.061(4)	0.053(3)	0.025(3)	-0.004(3)	-0.008(3)
C(15)	18f		0.2219(2)	0.3949(2)	0.0686(5)	0.049(3)	0.048(4)	0.075(4)	0.009(3)	0.001(3)	0.004(3)
C(16)	18f		0.2056(2)	0.4053(2)	-0.0315(5)	0.057(4)	0.046(3)	0.076(4)	0.018(3)	0.023(3)	0.006(3)
C(17)	18f		0.1595(2)	0.3736(2)	-0.0729(5)	0.059(4)	0.048(3)	0.049(3)	0.028(3)	0.017(3)	0.007(3)
C(18)	18f		0.1332(2)	0.3314(2)	-0.0073(4)	0.053(3)	0.047(3)	0.038(3)	0.026(3)	0.008(3)	-0.001(3)
C(19)	18f		0.0864(2)	0.2976(2)	-0.0480(4)	0.049(3)	0.047(3)	0.037(3)	0.027(3)	0.007(2)	0.001(2)
C(20)	18f		0.0670(2)	0.3073(2)	-0.1493(4)	0.053(3)	0.061(4)	0.046(3)	0.034(3)	-0.002(3)	0.003(3)
C(21)	18f		0.0214(2)	0.2723(2)	-0.1853(5)	0.068(4)	0.091(5)	0.048(3)	0.051(4)	-0.010(3)	-0.002(3)
C(22)	18f		-0.0021(2)	0.2314(2)	-0.1216(5)	0.054(4)	0.068(4)	0.063(4)	0.029(3)	-0.008(3)	-0.008(3)
C(23)	18f		0.0200(2)	0.2247(2)	-0.0205(5)	0.052(4)	0.062(4)	0.054(3)	0.028(3)	0.000(3)	-0.001(3)
C(24)	18f		0.1385(2)	0.3827(2)	-0.1752(5)	0.079(4)	0.064(4)	0.061(4)	0.041(4)	0.017(3)	0.018(3)
C(25)	18f		0.0943(2)	0.3510(2)	-0.2120(5)	0.083(5)	0.084(5)	0.051(3)	0.050(4)	-0.005(3)	0.010(3)

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