Preparation and *X*-Ray Crystal Structure of a Vanadium(III) Complex of Salicylaldehyde Hydrazone from Vanadium–Schiff Base Precursors†

David L. Hughes, G. Jeffery Leigh,* and J. Roger Sanders
A.F.R.C. Institute of Plant Science Research, Nitrogen Fixation Laboratory, University of Sussex, Brighton BN1 9RQ

Treatment of $[V(NH_2NHPh)_2(salen)]I$, $[VO(salen)]$ [salen = *N,N'*-ethylenebis(salicylideneiminate)], or a mixture of $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) and salicylaldehyde with anhydrous hydrazine under various conditions gives $[V(OC_6H_4CHNNH_2)_3]$, tris(salicylaldehyde hydrazonato)vanadium(III), of which the crystal structure is described.

We have been attempting to prepare hydrazine derivatives of vanadium-containing Schiff-base complexes as models for intermediates in the reduction of N_2 by vanadium-based nitrogenase,[1] and have reported[2] the preparation and structure of a bis(phenylhydrazine) compound of vanadium(III), $[V(NH_2NHPh)_2(salen)]I$ [salen = *N,N'*-ethylenebis(salicylideneiminate)(2−)]. The present report gives the results of our attempts to replace the phenylhydrazine ligands in this compound by hydrazine.

Results

Treatment of $[V(NH_2NHPh)_2(salen)]I$ with an excess of anhydrous hydrazine in methanol at +20 °C gives a solution which slowly deposits red crystals over a number of days. The magnetic susceptibility of these crystals (2.90 μ_B) is characteristic of a vanadium(III) compound, and their microanalysis and i.r. spectra suggest that they contain hydrazine [strong bands characteristic of ν(N–H) at 3360, 3310, and 3170 cm^{-1}]. They are almost insoluble in common organic solvents but react with non-co-ordinating acids such as $HBF_4 \cdot Et_2O$ to give salicylaldehyde azine (salazine, $HOC_6H_4CHNNCHC_6H_4OH$), consistent with their formulation as a complex containing salazine and hydrazine rather than salen(2−).

We subsequently found that red crystals with the same analysis and i.r. spectrum are formed when $[VO(salen)]$ is subjected to prolonged heating with an excess of hydrazine in acetonitrile–methanol under reflux, or when $[VCl_3(thf)_3]$ (thf = tetrahydrofuran) is treated at 20 °C in methanol with salicylaldehyde, salicylaldehyde hydrazone, or salazine, and an excess of hydrazine. Similar compounds can be made from $[VCl_3(thf)_3]$ by treatment with 3-methoxysalicylaldehyde or 5-bromosalicylaldehyde and an excess of hydrazine. These new syntheses established that the red crystals do not contain either phenylhydrazine (from the original starting material) or ethylenediamine (from breaking up of salen ligands).

We were unable to rationalise a structure on the basis of the red crystals containing only vanadium, salazine, and hydrazine, so we subjected selected crystals to *X*-ray analysis that revealed them to be tris(salicylaldehyde hydrazonato)vanadium(III). The bands in the 3400—3100 cm^{-1} region of the i.r. spectrum of the crystals may thus be assigned to ν(N–H) in the hydrazonate ligands.

Description of the Structure of $[V(C_7H_7N_2O)_3]$.—In the complex molecule, three chelating hydrazone ligands surround the V atom in a propeller-like arrangement. The pseudo-three-fold symmetry of these ligands is, however, spoilt, since one of the ligands is bound in the opposite direction to the other two (Figure). The resulting co-ordination about the vanadium atom has distorted-octahedral geometry, with the V–O and V–N distances showing rather wide ranges of values. The shortest V–O distance is opposite the longest V–N distance, a mild *trans* effect; in the other *trans* pairs, N(9b) is opposite N(9c), and O(1a) opposes O(1b). The mean dimensions, V–O 1.939(6) and V–N 2.14(3) Å, are somewhat longer than those found in another vanadium(III) complex $[V(NH_2NHPh)_2(salen)]I$, where V–O was 1.881(3) and V–N 2.082(5) Å;[2] the effects of hydrogen bonding, both intra- and inter-molecular (see below), may be the cause of the lengthened bonds in the present structure.

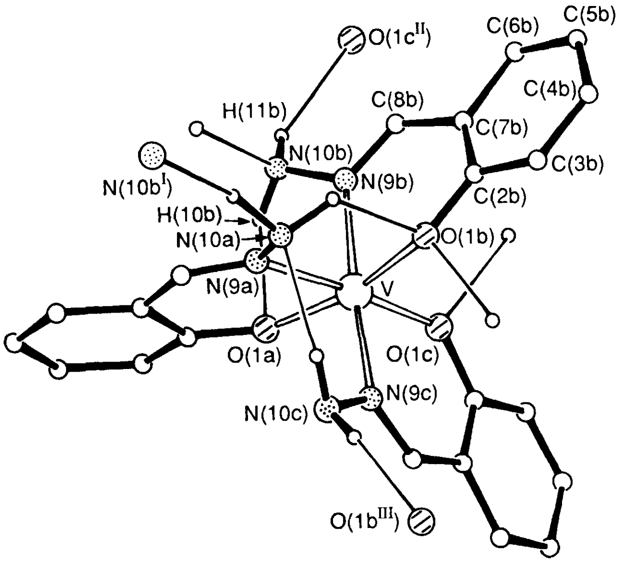

Figure. View of a molecule of $[V(C_7H_7N_2O)_3]$. The atom names in one ligand are shown; the other ligands are labelled similarly. Hydrogen bonds, intra- and inter-molecular, are indicated with thinner bonds. Roman superscripts denote symmetry relations which are defined in Table 2

There are also significant variations in the dimensions in the hydrazone ligands, probably resulting from inadequacies in the diffraction data. The mean values from the three ligands appear normal, *e.g.* O(1)–C(2) 1.323(11), C(8)–N(9) 1.278(5), N(9)–N(10) 1.410(3) Å, C(7)–C(8)–N(9) 126.0(6) and C(8)–N(9)–N(10) 115.9(3)°.

The striking feature in this structure is the hydrogen bonding. The two hydrogen atoms of each NH_2 group were located and

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Final atomic co-ordinates (fractional × 10^4) for $[V(C_7H_7N_2O)_3]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
V	2 203(2)	3 054(2)	4 315(2)
O(1a)	2 678(6)	4 314(6)	2 601(6)
C(2a)	2 115(10)	5 107(10)	1 776(11)
C(3a)	2 866(11)	5 942(11)	601(10)
C(4a)	2 286(14)	6 804(12)	−256(11)
C(5a)	952(14)	6 924(13)	40(12)
C(6a)	241(12)	6 159(11)	1 189(11)
C(7a)	792(11)	5 266(10)	2 066(10)
C(8a)	−89(10)	4 460(10)	3 283(11)
N(9a)	266(7)	3 665(8)	4 237(8)
N(10a)	−800(8)	2 922(8)	5 253(9)
H(10a)	−391(83)	2 691(84)	6 164(87)
H(11a)	−1 603(79)	3 496(77)	5 453(71)
O(1b)	1 519(6)	2 108(6)	6 138(6)
C(2b)	2 085(9)	2 240(10)	7 247(9)
C(3b)	1 646(10)	1 173(11)	8 362(10)
C(4b)	2 173(12)	1 291(12)	9 566(11)
C(5b)	3 115(12)	2 461(14)	9 686(11)
C(6b)	3 543(10)	3 521(11)	8 599(10)
C(7b)	3 053(9)	3 434(10)	7 353(10)
C(8b)	3 501(9)	4 665(10)	6 316(11)
N(9b)	3 223(7)	4 757(8)	5 123(9)
N(10b)	3 592(8)	6 086(8)	4 295(9)
H(10b)	3 728(77)	5 968(78)	3 390(78)
H(11b)	4 455(107)	6 810(109)	4 399(95)
O(1c)	3 884(5)	2 456(6)	4 279(6)
C(2c)	4 250(10)	1 514(9)	3 729(9)
C(3c)	5 609(10)	1 424(10)	3 697(8)
C(4c)	6 006(10)	494(11)	3 150(10)
C(5c)	5 101(12)	−427(11)	2 586(9)
C(6c)	3 751(11)	−380(10)	2 614(9)
C(7c)	3 292(9)	585(9)	3 183(8)
C(8c)	1 844(10)	524(10)	3 203(9)
N(9c)	1 228(8)	1 330(7)	3 639(7)
N(10c)	−208(10)	1 057(11)	3 541(9)
H(10c)	−775(67)	1 357(66)	4 235(65)
H(11c)	−492(68)	238(70)	3 647(62)

refined, and all are involved in hydrogen bonds. In each NH_2 group, H(10) forms an intramolecular bond which, in each case, connects the chelating ligand with the meridionally co-ordinated group in the complex, *e.g.* the hydrogen bond N(10a)–H(10a) ··· O(1b) completes the nearly planar, meridional arrangement of O(1a), N(9a), and O(1b). The three ligands are thus bound tightly together within the molecule.

Atom H(11) of each NH_2 group forms a hydrogen bond with an O or N atom of a neighbouring molecule; such bonds are formed in pairs, related by centres of symmetry, resulting in strong intermolecular interactions. Extensive sheets of hydrogen-bonded molecules are thus formed, corresponding to the flat, plane, shape of the crystal. Interactions between sheets are at normal van der Waals distances.

Discussion and Conclusions

In the presence of hydrazine there is an equilibrium between aldehydes, RCHO, and their hydrazones, $RCHNNH_2$, and azines, RCHNNCHR. It was found that if a 1 : 1 stoicheiometric ratio of hydrazine to aldehyde, or a 2 : 1 stoicheiometric ratio of hydrazine to V(salen) complex, was used in the preparations described here, salazine rather than salicylaldehyde hydrazone was produced; similarly, salazine rather than salicylaldehyde hydrazone was produced by acid decomposition of tris(salicylaldehyde hydrazonato)vanadium(III). Therefore a large excess of hydrazine, which produces a cation to balance halide ions derived from $[V(NH_2NHPh)_2(salen)]I$ or $[VCl_3(thf)_3]$, was used in the preparations. It was found that salazine does not ligate to vanadium when treated with $VOSO_4$ or $[VCl_3(thf)_3]$ in the absence of hydrazine.

The results show that hydrazine under sufficiently vigorous conditions is able to break up Schiff bases such as H_2salen (even when co-ordinated) by substituting an $=NNH_2$ or =N–N= group for the central $=NCH_2CH_2N=$ group. Reactions of Schiff-base compounds of vanadium and presumably of other metals with hydrazine may therefore give products in which the quadridentate Schiff-base ligand (which is usually considered inert and able to immobilise four co-ordination positions on the metal atom) is broken up. This effect is in addition to any effect of hydrazine and substituted hydrazines on the oxidation state of the metal.

Experimental

Reactions were carried out under dinitrogen in dried solvents; microanalyses were performed by Mr. C. J. Macdonald of this Laboratory. Magnetic moments were determined by the Faraday technique, with susceptibilities corrected using appropriate Pascal constants. Salicylaldehyde hydrazone and azine and ring-substituted analogues were made by mixing appropriate quantities of hydrazine and salicylaldehyde or substituted salicylaldehydes in boiling methanol or ethanol and allowing to cool to room temperature. The complexes $[V(NH_2NHPh)_2(salen)]I$,[2] [VO(salen)],[3] and $[VCl_3(thf)_3]$[4] were made as described elsewhere.

Tris(salicylaldehyde hydrazonato)vanadium(III).—(*a*) The complex $[V(NH_2NHPh)_2(salen)]I$ (2.64 g, 4 mmol) was stirred in methanol (80 cm^3) at 20 °C and hydrazine (0.64 g, 20 mmol) added. The suspension quickly dissolved giving a clear red solution that was filtered and set aside for 2 d. The red crystals (0.6 g, 1.3 mmol) that had formed were filtered off, washed with methanol and diethyl ether, and dried *in vacuo* (Found: C, 55.4; H, 4.8; N, 18.1. $C_{21}H_{21}N_6O_3V$ requires C, 55.3; H, 4.6; N, 18.4%).

(*b*) The complex [VO(salen)] (1.33 g, 4 mmol) was heated under reflux in MeCN (100 cm^3) and MeOH (25 cm^3) with hydrazine (1.6 g, 50 mmol) for 48 h, then cooled to give red crystals (0.3 g, 0.7 mmol) (Found: C, 54.7; H, 4.6; N, 18.2%).

(*c*) The complex $[VCl_3(thf)_3]$ (1.80 g, 5 mmol) was dissolved in methanol giving a green solution. Salicylaldehyde (1.83 g, 15 mmol) was added followed immediately by hydrazine (0.96 g, 30 mmol). The suspension dissolved giving a red solution from which 0.6 g (1.3 mmol) of crystals precipitated over 3 d (Found: C, 55.0; H, 4.7; N, 18.4%), $\mu_{eff.}$(293 K) = 2.90 μ_B. Salicylaldehyde hydrazone (15 mmol) or salazine (7.5 mmol) was also used in place of salicylaldehyde, the product being identified by its i.r. spectrum.

Also made by method (*c*) were *tris(3-methoxysalicylaldehyde hydrazonato)vanadium*(III) (Found: C, 52.2; H, 5.1; N, 14.9. $C_{24}H_{27}N_6O_6V$ requires C, 52.8; H, 4.9; N, 15.4%), $\mu_{eff.}$ = 2.95 μ_B, and *tris(5-bromosalicylaldehyde hydrazonato)vanadium*(III) (Found: C, 36.3; H, 2.7; N, 12.0. $C_{21}H_{18}Br_3N_6O_3V$ requires C, 36.4; H, 2.6; N, 12.0%), $\mu_{eff.}$ = 2.85 μ_B. In the latter case the reaction mixture was heated under reflux overnight because of the relative insolubility of 5-bromosalicylaldehyde.

Reaction of Tris(salicylaldehyde hydrazonato)vanadium(III) *with Acid*.—The complex $[V(C_7H_7N_2O)_3]$ (0.46 g, 1.0 mmol) was stirred in methanol (50 cm^3) and $HBF_4 \cdot Et_2O$ (0.5 g, 3.3 mmol) added. The suspension turned yellow; after 1 h it was warmed to 60 °C giving a yellow solution that gave crystals of salazine (0.15 g, 0.6 mmol) on cooling.

Table 2. Molecular dimensions (bond lengths in Å, angles in °) in $[V(C_7H_7N_2O)_3]$ with e.s.d.s in parentheses

(*a*) About the vanadium atom

V–O(1a)	1.935(6)	V–N(9a)	2.181(7)
V–O(1b)	1.950(6)	V–N(9b)	2.154(7)
V–O(1c)	1.931(6)	V–N(9c)	2.082(7)

O(1a)–V–N(9a)	83.6(3)	O(1b)–V–O(1c)	96.5(2)
O(1a)–V–O(1b)	166.5(3)	N(9b)–V–O(1c)	90.3(3)
N(9a)–V–O(1b)	85.8(3)	O(1a)–V–N(9c)	96.4(3)
O(1a)–V–N(9b)	86.9(3)	N(9a)–V–N(9c)	88.1(3)
N(9a)–V–N(9b)	93.3(3)	O(1b)–V–N(9c)	91.4(3)
O(1b)–V–N(9b)	85.6(3)	N(9b)–V–N(9c)	176.6(3)
O(1a)–V–O(1c)	94.7(3)	O(1c)–V–N(9c)	88.4(3)
N(9a)–V–O(1c)	175.9(3)		

(*b*) Bond lengths in the ligands a, b, and c

	a	b	c
O(1)–C(2)	1.301(10)	1.327(9)	1.338(9)
C(2)–C(3)	1.401(12)	1.389(11)	1.386(11)
C(2)–C(7)	1.403(12)	1.395(12)	1.409(11)
C(3)–C(4)	1.373(13)	1.400(12)	1.339(12)
C(4)–C(5)	1.398(15)	1.368(13)	1.388(12)
C(5)–C(6)	1.347(13)	1.365(13)	1.365(11)
C(6)–C(7)	1.387(12)	1.422(11)	1.412(11)
C(7)–C(8)	1.474(12)	1.440(12)	1.436(12)
C(8)–N(9)	1.271(10)	1.275(10)	1.289(10)
N(9)–N(10)	1.415(9)	1.406(9)	1.409(10)
N(10)–H(10)	1.06(9)	0.98(8)	1.04(7)
N(10)–H(11)	1.14(8)	1.02(10)	0.80(6)

(*c*) Angles in the ligands a, b, and c

	a	b	c
V—O(1)–C(2)	138.7(6)	130.0(6)	132.0(6)
O(1)–C(2)–C(3)	120.8(10)	118.7(9)	119.8(9)
O(1)–C(2)–C(7)	122.3(10)	122.6(9)	122.2(8)
C(3)–C(2)–C(7)	116.7(10)	118.7(9)	118.0(9)
C(2)–C(3)–C(4)	120.9(11)	120.6(10)	121.1(10)
C(3)–C(4)–C(5)	121.3(12)	121.3(10)	122.7(9)
C(4)–C(5)–C(6)	118.1(11)	118.6(10)	117.8(9)
C(5)–C(6)–C(7)	121.9(11)	122.0(10)	121.1(10)
C(2)–C(7)–C(6)	120.9(11)	118.9(9)	119.2(9)
C(2)–C(7)–C(8)	121.7(9)	124.5(9)	123.8(9)
C(6)–C(7)–C(8)	117.3(10)	116.2(9)	117.0(9)
C(7)–C(8)–N(9)	126.4(9)	124.9(9)	126.7(9)
V–N(9)–C(8)	127.0(7)	125.1(7)	125.3(7)
V–N(9)–N(10)	116.4(6)	118.4(6)	118.8(6)
C(8)–N(9)–N(10)	115.6(8)	116.5(8)	115.7(8)
N(9)–N(10)–H(10)	111(5)	107(5)	116(4)
N(9)–N(10)–H(11)	115(4)	122(6)	107(5)
H(10)–N(10)–H(11)	104(6)	105(7)	107(7)

(*d*) Hydrogen bonding dimensions

	N···N/O distance	H···N/O distance	N–H···N/O angle
N(10a)–H(10a)···O(1b)	2.787(10)	2.14(8)	117(6)
N(10a)–H(11a)···N(10b^{I})	3.251(11)	2.16(8)	159(6)
N(10b)–H(10b)···O(1a)	2.821(11)	2.11(8)	127(6)
N(10b)–H(11b)···O(1c^{II})	3.205(10)	2.29(10)	148(8)
N(10c)–H(10c)···N(10a)	3.020(13)	2.11(7)	145(5)
N(10c)–H(11c)···O(1b^{III})	3.137(12)	2.34(7)	174(6)

Roman superscripts denote the symmetry operations: I $-x, 1-y, 1-z$; II $1-x, 1-y, 1-z$; III $-x, -y, 1-z$.

Reaction of H_2salen *with Hydrazine.*—The compound H_2salen (0.53 g, 2 mmol) and hydrazine (0.32 g, 10 mmol) were stirred in methanol for 3 d; $HBF_4{\cdot}Et_2O$ (2 g, excess) was added, precipitating salazine.

Crystal Structure Analysis of $[V(C_7H_7N_2O)_3]$.—*Crystal data.* $C_{21}H_{21}N_6O_3V$, $M = 456.4$, triclinic, space group $P\bar{1}$ (no. 2), $a = 10.019(1)$, $b = 10.283(1)$, $c = 10.424(1)$ Å, $\alpha = 77.828(7)$, $\beta = 87.434(8)$, $\gamma = 104.183(9)°$, $U = 1\,012.6$ Å^3, $Z = 2$, $D_c = 1.497$ g cm^{-3}, $F(000) = 472$, $\mu(\text{Mo-}K_\alpha) = 5.1$ cm^{-1}, $\lambda(\text{Mo-}K_{\bar{\alpha}}) = 0.710\,69$ Å.

Crystals are deep red, thin laths; all are twinned, each by a pairing of two laths along their long, thin, sides. One such pair was sliced in half along the twinning plane giving a single sliver, 0.17 × 0.05 × 0.01 mm; this was mounted on a glass fibre with epoxy resin. After preliminary photographic examination, the crystal was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell dimensions (from the settings of 25 reflections, with θ in the range 6—9°, each centred in four orientations) and measurement of diffraction intensities (to $\theta_{max.} = 20°$). During processing, intensities were corrected for Lorentz-polarisation effects and to eliminate negative intensities (by Bayesian statistical methods). There was no deterioration of the crystal during the data collection, and no absorption correction was applied.

1 879 Independent reflections (of which 1 052 had $I > 2\sigma_I$) were entered into the SHELX program system.[5] An electron-density map based on the V atom (located from the Patterson map) showed the whole structure clearly. During the refinement process, by full-matrix least-squares methods, hydrogen atoms of C–H groups were included in idealised positions, and the N–H hydrogen atoms, all located in difference maps, were refined independently. All the non-hydrogen atoms were allowed anisotropic thermal parameters. Refinement reached convergence with $R = 0.081$, $R_g = 0.053$[5] for 1503 reflections (those with $I > \sigma_I$) weighted $w = \sigma_F^{-2}$. This rather high value for R probably results from the overall weak diffraction intensities measured from the small crystal used. There were no features of significance in the final difference map.

Scattering-factor curves for neutral atoms were taken from ref. 6. Computer programs, in addition to SHELX, have been listed in Table 4 of ref. 7 and were run on the MicroVAX II computer in this Laboratory. Final atomic co-ordinates are in Table 1 and selected molecular dimensions in Table 2.

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

References

1 R. L. Robson, R. R. Eady, T. H. Richardson, R. W. Miller, M. Hawkins, and J. R. Postgate, *Nature* (*London*), 1986, **322**, 388.
2 A. Hills, D. L. Hughes, G. J. Leigh, and J. R. Sanders, *J. Chem. Soc., Dalton Trans.*, in the press.
3 M. Mazzanti, S. Gambarotta, C. Floriani, A. Chiesi-Villa, and C. Guastini, *Inorg. Chem.*, 1986, **25**, 2308.
4 G. W. A. Fowles, P. T. Greene, and T. E. Lester, *J. Inorg. Nucl. Chem.*, 1967, **29**, 2365.
5 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
6 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
7 S. N. Anderson, R. L. Richards, and D. L. Hughes, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

Received 23*rd April* 1990; *Paper* 0/01792B