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Synthesis, Structure, ESR Spectra, and Redox Properties of (*N*,*N'*-Ethylenebis(thiosalicylideneaminato))oxovanadium(IV) and of Related {S,N} Chelates of Vanadium(IV)

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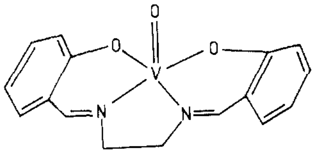
The synthesis, structure, spectra, and redox properties of $V^{IV}O$(tsalen) (tsalen is *N,N'*-ethylenebis(thiosalicylideneaminate)) and of related oxovanadium(IV) {S,N} Schiff-base chelates are described. The synthesis and properties of the six-coordinate (trigonal-prismatic) non-oxo vanadium(IV) complex $[V^{IV}(\text{sal-NSO})_2]$ (sal-NSO is *N*-(2-hydroxyphenyl)thiosalicylideneaminate) are also described. $V^{IV}O$(tsalen) crystallizes in the monoclinic space group $P2_1/c$ with the following unit cell dimensions (at 20 °C): $a = 7.069$ (4) Å, $b = 9.105$ (5) Å, $c = 24.181$ (9) Å, $\beta = 90.62$ (1)°, $Z = 4$. The molecule possesses a square-pyramidal geometry with an average V—S distance of 2.346 Å, a V—N distance of 2.080 Å, and a V=O distance of 1.598 (6) Å. (The vanadium atom lies 0.608 (1) Å out of the ligand best plane.) The geometry is generally similar to that in $V^{IV}O$(salen). A detailed comparison of the ESR and electrochemical features of $V^{IV}O$(tsalen) and $V^{IV}O$(salen) is given and provides donor-atom-dependent data useful for probing vanadium(IV) in biological and crude oil environments. The ESR and electrochemical properties of the non-oxo complex $[V^{IV}(\text{sal-NSO})_2]$ are also described and are different in detail from those of $V^{IV}O$(tsalen).

Introduction

Some years ago we investigated the synthesis[1] and electrochemistry[2] of Schiff-base vanadium(III) and vanadium(IV) complexes of types $[V^{III}(\text{salen})Cl(py)]$,[1] $V^{IV}(\text{salen})Cl_2$,[2] and $V^{IV}O$(salen) (**1**).[2] Subsequent reports by a number of groups on these and on the analogous acen complexes have largely substantiated our results and have extended knowledge of the structures of many of these complexes and of their oxovanadium(V) counterparts.[3-8] Electrochemical studies of $V^{IV}O$(salen)[2,6-8] showed a reversible one-electron oxidation to the oxovanadium(V) species $V^VO(\text{salen})^+$, and this complex has recently been structurally characterized in crystals of $V^VO(\text{salen})ClO_4$.[8] This monooxovanadium(V) entity, analogous to oxomolybdenum(V), is rare[9] in comparison to the dioxovanadium(V) species, VO_2^+.



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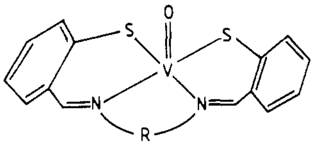
We have been particularly interested in synthesizing corresponding {S,N} chelates of vanadium of type $V^{IV}O$(tsalen) (**2a**) not only so that we could compare their properties with those of the salen species but also because {S,N} chelates of vanadium were virtually unknown at the beginning of this study. Further, these compounds contain vanadium–thiophenolate bonds and are potentially useful as bioinorganic vanadium model compounds[10] and for an understanding of vanadium in crude oils.[11] The first crystal structure of a {S,N}-chelated species has just become available through the work of Christou et al.[12] on the μ-oxo complex $(V^{III}(SCH_2CH_2NMe_2)_2)_2O$. Sulfur–vanadium chelates, in general, have only recently been studied in any detail, e.g. $[V^{IV}O(SCH_2CH_2S)_2]^{2-}$.[13-15] Sulfido vanadium(IV) and -(V) compounds have also become available in chelated species such as $[S{=}V^{IV}(SCH_2CH_2S)_2]^{2-}$ [13-15] and in thiovanadate compounds.[16-18] Clearly, the traditional view of vanadium preferring to bind to O,N-donors must be modified in view of the rich and varied S-donor chemistry that is now emerging.



2a, R = $(CH_2)_2$
b, R = $(CH_2)_3$
c, R = $o\text{-}C_6H_4$
d, R = $o\text{-}4,5\text{-}Me_2\text{-}C_6H_2$

The synthesis, redox, and ESR features of complexes **2** and of the non-oxo bis(tridentate) vanadium(IV) derivative $V^{IV}(\text{sal-NSO})_2$ (**3**) are reported here, and comparisons are made with the salicylideneamine analogues. Vanadium(III)–tsalen complexes will be described separately.

Experimental Section

Abbreviations: salen^{2-} = *N,N'*-ethylenebis(salicylideneaminate); acen^{2-} = *N,N'*-ethylenebis(acetylacetone iminate); tsalen^{2-} = *N,N'*-ethylenebis(thiosalicylideneaminate); tsaltn^{2-} = *N,N'*-trimethylenebis(thiosalicylideneaminate); tsalphen^{2-} = *N,N'*-*o*-phenylenebis(thio-

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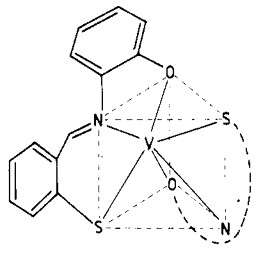
(1) Murray, K. S.; Simm, G. R.; West, B. O. *Aust. J. Chem.* **1973**, *26*, 991.
(2) (a) Murray, K. S.; Koh, S., unpublished data. (b) Koh, S. B.Sc. Honors Thesis, Monash University, 1982.
(3) Mazzanti, M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 2308.
(4) McNeese, T. J.; Mueller, T. E. *Inorg. Chem.* **1985**, *24*, 2981.
(5) Mazzanti, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 4158.
(6) Kapturkiewicz, A. *Inorg. Chim. Acta* **1981**, *53*, L77.
(7) Bonadies, J. A.; Carrano, C. J. *J. Am. Chem. Soc.* **1986**, *108*, 4088.
(8) Bonadies, J.; Butler, W. M.; Pecoraro, V. L.; Carrano, C. J. *Inorg. Chem.* **1987**, *26*, 1218.
(9) Another structurally characterized VO^{3+} complex of a tridentate hydrazone ligand has recently been reported: Diamantis, A. A.; Frederiksen, J. M.; Salam, Md. A.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1986**, *39*, 1081. One of the first chemically well-characterized examples was $VO(acac)_2Cl$: Fackler, J. P.; Anderson, S.; Jones, J. P.; Kopperl, S. J. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 49.
(10) See e.g.: (a) Chasteen, N. D. *Struct. Bonding (Berlin)* **1983**, *53*, 107. (b) Kustin, K.; McLeod, G. C.; Gilbert, T. R.; Briggs, L. B. R., IV. *Struct. Bonding (Berlin)* **1983**, *53*, 140.
(11) (a) Biggs, W. R.; Fetzer, J. C.; Brown, R. J.; Reynolds, J. G. *Liq. Fuels Technol.* **1985**, *3*, 397. (b) Dickson, F. E.; Kunesh, C.; McGinnis, E. L.; Petrakis, L. *Anal. Chem.* **1972**, *44*, 978.
(12) Money, J. K.; Folting, K.; Huffmann, J. C.; Christou, G. *Inorg. Chem.* **1987**, *26*, 944.
(13) Szeymies, D.; Krebs, B.; Henkel, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 804.
(14) Money, J. K.; Huffmann, J. C.; Christou, G. *Inorg. Chem.* **1985**, *24*, 3297.
(15) Money, J. K.; Folting, K.; Huffmann, J. C.; Collison, D.; Temperley, J.; Mabbs, F. E.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4583.
(16) Do, Y.; Simhon, E. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 6731.
(17) Kovacs, J. A.; Holm, R. H. *Inorg. Chem.* **1987**, *26*, 702, 711 and references therein.
(18) Money, J. K.; Nicholson, J. R.; Huffmann, J. C.; Christou, G. *Inorg. Chem.* **1986**, *25*, 4072.

0020-1669/88/1327-0034$01.50/0



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salicylideneaminate); tsal-4,5-Me$_2$-phen^{2-} = *N*,*N*′-4,5-dimethylphenylenebis(thiosalicylideneaminate); acac$^-$ = acetylacetonate; sacac$^-$ = monothioacetylacetonate; sacsac$^-$ = dithioacetylacetonate; sal-NSO^{2-} = *N*-(2-hydroxyphenyl)thiosalicylideneaminate; edt^{2-} = ethane-1,2-dithiolate; mquin$^-$ = 2-methylquinolin-8-olate; DTBC^{2-} = 3,5-di-*tert*-butylcatecholate; detc = diethyldithiocarbamate.

Synthesis. In general the preparations of the vanadium(IV) and vanadium(III) complexes were carried out under an atmosphere of purified nitrogen, although the vanadium(IV) products were usually stable when dry. The starting materials V^{IV}O(acac)$_2$,[19] V^{IV}O(salen),[2] [V^{III}(dmso)$_6$](BF$_4$)$_3$,[20] 2-mercaptobenzaldehyde,[21] and *N*-(2-hydroxyphenyl)thiosalicylideneamine[22] were prepared and purified as described previously. Solvents were degassed with nitrogen before use.

V^{IV}O(tsalen) (2a). 2-Methoxyethanol solutions of 2-mercaptobenzaldehyde (0.086 g, 0.62 mmol) and ethylenediamine (0.018 g, 0.30 mmol) were added to VO(acac)$_2$ (0.082 g, 0.31 mmol) in 15 mL of 2-methoxyethanol. The resulting red-brown solution was refluxed gently for 4 h, and then 5 mL of petroleum ether was added. The solution, which was then stored at 0 °C, eventually yielded well-formed flaky dark green crystals, which were filtered and washed with ethanol. The yield was 0.029 g (26%). Anal. Calcd for C$_{16}$H$_{14}$N$_2$OS$_2$V: C, 52.6; H, 3.9; N, 7.7. Found: C, 53.0; H, 3.9; N, 7.9. Mass spectrum: *m*/*e* 365 (M$^+$). IR spectrum: ν(V=O) 975 cm^{-1}. Magnetic moment: μ = 1.76 μ_B. The crystals obtained by this route, though well-formed, could not be grown (of sufficient thickness) to be suitable for crystallographic measurements despite numerous crystal-growing attempts. Suitable crystals were in fact obtained from an attempted preparation of vanadium(III) species using [V^{III}(dmso)$_6$](BF$_4$)$_3$ as starting material. A small quantity of V^{IV}O(tsalen) crystals coprecipitated with the vanadium(III) product and could be readily separated. These crystals displayed properties identical with those obtained from V^{IV}O(acac)$_2$.

V^{IV}O(tsaltn) (2b). To an ethanolic solution (10 mL) of 2-mercaptobenzaldehyde (0.083 g, 0.6 mmol) was added 1,3-diaminopropane (0.022 g, 0.30 mmol) in 5 mL of ethanol. The resulting orange solution was stirred for 20 min. To this preformed tsaltn-H$_2$ ligand solution was then added VO(acac)$_2$ (0.081 g, 0.31 mmol) in 10 mL of ethanol. The red-brown mixture was refluxed for 4 h, during which time a brown powder formed. The product was filtered and washed with ethanol. The yield was 0.018 g (16%). Anal. Calcd for C$_{17}$H$_{16}$N$_2$OS$_2$V: C, 53.8; H, 4.3; N, 7.4. Found: C, 53.7; H, 4.3; N, 7.4. Mass spectrum: *m*/*e* 379 (M$^+$). IR spectrum: ν(V=O) 840 cm^{-1}.

V^{IV}O(tsalphen) (2c). 2-Methoxyethanol solutions of 2-mercaptobenzaldehyde (0.131 g, 0.95 mmol) and *o*-phenylenediamine (0.051 g, 0.47 mmol) were added to VO(acac)$_2$ (0.130 g, 0.49 mmol) in 20 mL of 2-methoxyethanol. The resulting red-brown solution was refluxed for 30 min, during which time small dark brown crystals formed. The product was filtered and washed with ethanol. The yield was 0.078 g (40%). Anal. Calcd for C$_{20}$H$_{14}$N$_2$OS$_2$V: C, 58.1; H, 3.4; N, 6.8. Found: C, 58.5; H, 3.8; N, 6.5. Mass spectrum: *m*/*e* 413 (M$^+$). IR spectrum: ν(V=O) 970 cm^{-1}. Magnetic moment: μ = 1.87 μ_B.

V^{IV}O(tsal-4,5-Me$_2$-phen) (2d). Ethanolic solutions (10 mL) of 2-mercaptobenzaldehyde (0.083 g, 0.60 mmol) and 4,5-dimethyl-*o*-phenylenediamine (0.041 g, 0.30 mmol) were added to VO(acac)$_2$ (0.084 g, 0.32 mmol) in 10 mL of ethanol. The resulting red-brown solution yielded a brown powder after refluxing for 20 min, which was filtered and washed with ethanol. The yield was 0.044 g (33%). Anal. Calcd for C$_{22}$H$_{18}$N$_2$OS$_2$V: C, 59.9; H, 4.2; N, 6.4. Found: C, 60.1; H, 4.3; N, 6.3. Mass spectrum: *m*/*e* 441 (M$^+$). IR spectrum: ν(V=O) 970 cm^{-1}. Magnetic moment: μ = 1.80 μ_B.

V^{IV}(sal-NSO)$_2$ (3). VO(acac)$_2$ (0.206 g, 0.78 mmol) was added as a solid to a methanolic solution (20 mL) of *N*-(2-hydroxyphenyl)thiosalicylideneimine (0.346 g, 1.51 mmol). The resulting brown solution was refluxed for 30 min, during which time dark brown microcrystals were formed. These were filtered and washed with methanol. Anal. Calcd for C$_{26}$H$_{18}$N$_2$O$_2$S$_2$V: C, 61.77; H, 3.60; N, 5.54. Found: C, 61.80; H, 3.69; N, 5.40. Mass spectrum: *m*/*e* 505 (M$^+$). Magnetic moment: μ = 1.60 μ_B.

Table I. Crystallographic Data for V^{IV}O(tsalen) (**2a**)

formula	C$_{16}$H$_{14}$N$_2$OS$_2$V
fw	365.4
cryst syst	monoclinic
cryst habit	bladed
cryst size, mm	0.03 × 0.26 × 0.24
space group	$P2_1/c$
syst absences	$h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$
temp, °C	20
a, Å	7.069 (4)
b, Å	9.105 (5)
c, Å	24.181 (9)
β, deg	90.62 (1)
Z	4
V, Å^3	1556 (1)
D_{calcd}, g cm^{-3}	1.56
D_{measd}, g cm^{-3}	1.55 (1)
radiation (monochromated in incident beam)	Mo Kα (0.7107 Å)[a]
μ, cm^{-1}	8.7[b]
transmission factors (max, min)[e]	0.932, 0.791
data collecn instrum	Philips PW1100
scan speed, deg s^{-1}	0.05
scan width, deg	±(0.70 + 0.3 tan θ)
scan method	ω
collection range, deg	$6 < 2\theta \leq 60$
data collected	$\pm h,k,l$
total no. of unique data	4277
data used for refinement ($I \geq 3\sigma(I)$)[e]	1246
no. of params refined	107
quality-of-fit indicator	1.881[d]
R	0.060
R_w[c,e]	0.054
largest peak, e Å^{-3}	0.54

[a] Graphite monochromator. [b] Ibers, J. A., Hamilton, W. C., Eds. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. [c] $R_w = \sum w^{1/2}(||F_o| - |F_c||)/\sum w^{1/2}|F_o|$, where $w = [\sigma^2(F_o)]^{-1}$. [d] Quality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$. [e] Sheldrick, G. M. "Shelx-76 Program System"; University of Cambridge: Cambridge, England, 1976.

Zn(tsalen) was synthesized in air by adding a cold ethanolic solution (15 mL) of Zn(CH$_3$CO$_2$)$_2$·2H$_2$O (0.12 g, 0.55 mmol) to the orange-yellow solution obtained by mixing ethylenediamine (0.03 g, 0.5 mmol) and 2-mercaptobenzaldehyde (0.14 g, 1 mmol) in cold ethanol (20 mL). Fine yellow microcrystals of Zn(tsalen) were deposited within 5 min, and these were filtered and washed with ethanol; yield 0.13 g (73%). Anal. Calcd for C$_{16}$H$_{14}$N$_2$S$_2$Zn: C, 52.8; H, 3.9; N, 7.7. Found: C, 52.9; H, 3.6; N, 7.9.

X-ray Crystallography and Structure Solution. Data were collected at 20 °C on a Philips PW1100 diffractometer. Full details of the diffractometry and computational procedures employed are available elsewhere.[23] Data collection parameters are summarized in Table I. The structure was solved by conventional Patterson and Fourier methods. Full-matrix least-squares refinement employing anisotropic thermal parameters for V and S and isotropic thermal parameters for all other atoms (a single isotropic thermal parameter was used for hydrogen atoms, which were positioned in geometrically idealized positions: C–H = 0.97 Å) (refined to 0.066 (8) Å^2) reduced *R* and R_W to the values given in Table I. Final atomic parameters are given in Table II. Hydrogen atom coordinates, anisotropic thermal parameters, all bond lengths and angles, and observed and calculated structure factors are given in the supplementary material (Tables S1–S3).

Other Measurements. Infrared spectra were recorded as Nujol mulls on a Jasco IRA-2 spectrophotometer. UV-visible spectra were obtained in DMF solutions on a Varian SuperScan 3 spectrophotometer. X-Band ESR spectra were recorded on a Varian E12 spectrometer using frozen-solution samples. Magnetic susceptibilities were measured by using the Faraday method. Elemental analyses were performed by the Australian Microanalytical Service, Melbourne, Australia. Mass spectra were measured on a VG Micromass 7070F instrument. Cyclic voltam-

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(19) Rowe, R. A.; Jones, M. M. *Inorg. Synth.* **1957**, *5*, 113.
(20) Nichols, P., private communication, Monash University.
(21) Marini, P. J.; Murray, K. S.; West, B. O. *J. Chem. Soc., Dalton Trans.* **1983**, 143.
(22) Muto, Y. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1242.
(23) Fallon, G. D.; Gatehouse, B. M. *J. Solid State Chem.* **1980**, *34*, 193.

Table II. Atomic Parameters for VO(tsalen) (**2a**)[a]

atom	x	y	z	U(iso), Å²
V	0.0466 (2)	0.7279 (1)	0.4369 (1)	0.0310 (5)[b]
S(1)	0.2425 (3)	0.5935 (3)	0.4970 (1)	0.0381 (8)[b]
S(2)	0.1374 (3)	0.5529 (3)	0.3708 (1)	0.0456 (9)[b]
N(1)	−0.1169 (8)	0.7847 (7)	0.5045 (2)	0.033 (2)
N(2)	−0.2184 (9)	0.7435 (7)	0.3990 (3)	0.036 (2)
O	0.1545 (8)	0.8765 (7)	0.4216 (2)	0.048 (2)
C(1)	0.2545 (12)	0.6847 (9)	0.5604 (3)	0.035 (2)
C(2)	0.4172 (13)	0.6643 (9)	0.5929 (4)	0.042 (2)
C(3)	0.4354 (14)	0.7300 (10)	0.6444 (4)	0.056 (3)
C(4)	0.2940 (13)	0.8135 (10)	0.6654 (4)	0.053 (3)
C(5)	0.1298 (13)	0.8346 (9)	0.6352 (4)	0.049 (3)
C(6)	0.1082 (11)	0.7728 (9)	0.5820 (3)	0.030 (2)
C(7)	−0.0735 (12)	0.8012 (9)	0.5552 (3)	0.038 (2)
C(8)	−0.3200 (13)	0.8136 (10)	0.4901 (4)	0.052 (3)
C(9)	−0.3349 (14)	0.8456 (11)	0.4321 (4)	0.060 (3)
C(10)	−0.2924 (14)	0.6884 (9)	0.3554 (4)	0.045 (3)
C(11)	−0.2084 (13)	0.5946 (10)	0.3148 (4)	0.043 (2)
C(12)	−0.3266 (14)	0.5640 (10)	0.2685 (4)	0.054 (3)
C(13)	−0.2662 (14)	0.4736 (11)	0.2267 (4)	0.060 (3)
C(14)	−0.0897 (14)	0.4150 (11)	0.2286 (4)	0.057 (3)
C(15)	0.0263 (13)	0.4403 (10)	0.2734 (3)	0.050 (3)
C(16)	−0.0266 (12)	0.5323 (9)	0.3172 (3)	0.039 (2)

[a] Esd's are given in parentheses. [b] U(eq) for V and S: $^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j \vec{a}_i \cdot \vec{a}_j$.

Table III. UV-Visible Spectral Bands of $V^{IV}O(S_2N_2)$, $V^{IV}O(O_2N_2)$, and $V^{IV}O(S)_4$ Donor Sets

complex[a]	λ, nm (ε, L mol⁻¹ cm⁻¹)			
$V^{IV}O$(tsalen) (**2a**)	670 (107)	594 (181)	391 (8500)	
$V^{IV}O$(salen) (**1**)		587 (123)[b]	363 (6075)	
$[V^{IV}O(SCH_2CH_2S)_2]^{2-}$	622 (78)	550 sh (50)	400 (500)	312 (3600)
$V^{IV}O$(tsaltn) (**2b**)			405[c]	
$V^{IV}O$(tsalphen) (**2c**)		600 br (132)	468 (3453)	348 (14 101)
$V^{IV}O$(tsal-4,5-Me_2phen) (**2d**)		600 br (176)	468 (5740)	346 (28 900)
V^{IV}(sal-NSO)$_2$ (**3**)		532 (2131)		350 (9964)

[a] In DMF solution at 20 °C. [b] Shoulder also at 474 (50). [c] Only partly soluble.

metry measurements were made on a BAS 100 instrument. The working electrode was a stationary-disk platinum electrode, and the auxiliary electrode was a platinum wire. All measurements were done in dry and degassed DMF with tetrabutylammonium perchlorate (TBAP, 0.11 M) as supporting electrolyte. Potentials were recorded versus the saturated calomel electrode (SCE).

Results and Discussion

Synthesis and Characterization. Complexes of type **2** were prepared by displacement of acacH from $V^{IV}O(acac)_2$ on reaction with 2-mercaptobenzaldehyde and the appropriate diamine in refluxing ethanol or 2-methoxyethanol solutions. $V^{IV}O(acac)_2$ provides a convenient source of VO^{2+}, and the reaction conditions are relatively mild in comparison to those of other displacement reactions in which $V^{IV}O(acac)_2$ has been used.[5,24] A very recent report of the synthesis of the {S,N}-chelated complex $V^{IV}O(SCH_2CH_2NH_2)_2$ by this method used even milder conditions, i.e. room temperature.[12] The present complexes are stable in air in the crystalline state. Each characteristically displays a ν(V=O) frequency in the IR spectrum at ca. 970 cm⁻¹ except for $V^{IV}O$(tsaltn), in which the band is at 840 cm⁻¹, indicative of weak - -V=O- -V=O- - interactions in the solid state as was noted in the structure of $V^{IV}O$(saltn).[25] The magnetic moments are as expected for d¹ monomeric species, while the frozen-solution ESR spectra show the typical hyperfine splitting and anisotropic line shapes of VO^{2+} chelates (discussed in further detail below). The complexes are green or brown. Crystals of **2a** show a green/brown pleochroism under a microscope. The optical spectral bands of DMF solutions are given in Table III and are compared with those of $V^{IV}O$(salen). Strong charge-transfer bands occur in the region 470–360 nm. d–d transitions are evident in $V^{IV}O$(tsalen) at 670 and 594 nm compared to 587 nm in $V^{IV}O$(salen). Assuming that the ~590-nm bands are assigned to the same transition, it would appear that 10*Dq* values are similar for the $VO(O_2N_2)$ and $VO(S_2N_2)$ chromophores.

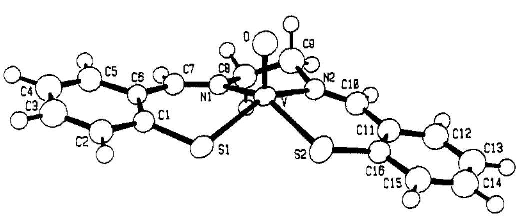

Figure 1. Molecular structure and numbering scheme of $V^{IV}O$(tsalen) (**2a**).

Table IV. Bond Lengths (Å) for VO(tsalen) (**2a**)[a]

V–S(1)	2.342 (3)	S(2)–C(16)	1.741 (9)
V–S(2)	2.350 (3)	N(1)–C(7)	1.27 (1)
V–N(1)	2.078 (6)	N(1)–C(8)	1.50 (1)
V–N(2)	2.082 (7)	N(2)–C(9)	1.48 (1)
V–O	1.598 (6)	N(2)–C(10)	1.27 (1)
S(1)–C(1)	1.745 (9)		

[a] Esd's are given in parentheses.

Table V. Bond Angles (deg) for VO(tsalen) (**2a**)[a]

S(1)–V–S(2)	84.5 (1)	S(2)–V–N(1)	149.5 (2)
N(1)–V–N(2)	79.9 (2)	S(2)–V–N(2)	89.9 (2)
O–V–S(1)	107.8 (2)	V–S(1)–C(1)	108.6 (3)
O–V–S(2)	106.4 (2)	V–S(2)–C(16)	113.3 (3)
O–V–N(1)	104.0 (3)	V–N(1)–C(7)	131.2 (5)
O–V–N(2)	105.6 (3)	V–N(1)–C(8)	113.6 (5)
S(1)–V–N(1)	88.4 (2)	V–N(2)–C(9)	107.9 (5)
S(1)–V–N(2)	146.3 (2)	V–N(2)–C(10)	134.2 (6)

[a] Esd's are given in parentheses.

The bis(tridentate) non-oxo vanadium(IV) complex **3** was synthesized by reaction of $V^{IV}O(acac)_2$ with 2 mol equiv of the ligand H_2sal-NSO in dry methanol under a nitrogen atmosphere. This dark brown complex is similar to an analogous ONO-bonded complex reported by Diamantis et al.[26,27] The ability to displace the oxo group as well as the acac group in such reactions has been used before in preparing tris(catecholate) vanadium(IV) complexes[28] and depends on the ligand being dianionic and possessing strongly electron donating (σ and π) donor atoms. We,[29] and others,[30] have recently used the same principle to obtain bis(tridentate) Mn^{IV} complexes. The stability of these ML_2 species is related to the fact that the two tridentate ligands can provide the electron density needed to stabilize the non-oxo metal(IV) moiety. This electron density is provided primarily by four strongly basic oxygens (of the ONO ligands) or two oxygens and two sulfurs (of the NSO ligands). Steric and π-bonding effects provided by the two coplanar chelate rings within the tridentate sal-NSO^{2-} ligand also aid in stabilizing the ML_2 species. Care is required in using dry solvents and anaerobic reaction conditions for the synthesis of $V^{IV}L_2$ complexes of type **3** in order to prevent oxidation and hydrolysis occurring to yield oxovanadium(V)

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(24) Ramiah, K.; Martin, D. F. *J. Inorg. Nucl. Chem.* **1965**, *27*, 1663.

(25) (a) Farmer, R. L.; Urbach, F. L. *Inorg. Chem.* **1974**, *13*, 587. (b) Mathew, M.; Carty, A. J.; Palenik, G. J. *J. Am. Chem. Soc.* **1970**, *92*, 3197.

(26) (a) Diamantis, A. A.; Snow, M. R.; Vanzo, J. A. *J. Chem. Soc., Chem. Commun.* **1976**, 264. (b) Diamantis, A. A.; Salam, Md. A., unpublished data.

(27) Diamantis, A. A.; Raynor, J. B.; Rieger, P. H. *J. Chem. Soc., Dalton Trans.* **1980**, 1731.

(28) Cooper, S. R.; Yoh, Y. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092.

(29) Humphrey, D.; Murray, K. S., unpublished work, 1986.

(30) (a) Kessissoglou, D. P.; Li, X.; Butler, W. M.; Pecoraro, V. L. *Inorg. Chem.* **1987**, *26*, 2487. (b) Diamantis, A. A., personal communication, 1986.

Table VI. Comparison of Selected Bond Distances (Å) and Angles (deg)

	$V^{IV}O$(tsalen)	$V^{IV}O$(salen)[a]	$[V^{IV}O(edt)_2]^{2-}$[b]
V=O	1.598 (6)	1.590 (1)	1.625 (2)
V—O(av)		1.921	
V—S(av)	2.346		2.378
V—N(av)	2.080	2.050	
V-plane[c]	0.608 (1)	0.609[a]	0.668
S-V-S(av)[d]	84.5 (1)		85.6
N-V-N	79.9 (2)	78.48 (5)	
S-V-N(av)[d]	89.1		
O-V-N(av)[d]		87.2	

[a] Molecule A.[7] [b] $(Me_4N)Na[VO(edt)_2]\cdot 2EtOH$.[14] [c] Distance of vanadium from best plane of "in-plane" donors. [d] "Cis" angles.

Table VII. ESR Parameters[a]

complex	donor set	$g_\parallel$	$g_\perp$	$-A_\parallel$, 10^4 cm^{-1}	$-A_\perp$ 10^4 cm^{-1}
2a[g]	$VO(N_2S_2)$	1.978	1.986	148	51
2b	$VO(N_2S_2)$	1.966	1.975	140	37
2c	$VO(N_2S_2)$	1.967	1.987	145	51
2d	$VO(N_2S_2)$	1.967	1.989	145	52
1	$VO(N_2O_2)$[b]	1.951	1.985	159	59
$VO(mquin)_2$	$VO(N_2O_2)$[c,d]	1.949	1.985	157	53
$[VO(edt)_2]^{2-}$	$VO(S_4)^{2-}$[c,e]	1.976	1.977	134	40
3	$V(O_2N_2S_2)$	1.962	~1.99[f]	124	~55[f]

[a] In frozen DMF. [b] References 7, 32 and 33. [c] Small rhombicity in $g_\perp$, $A_\perp$. [d] Reference 34. [e] References 14 and 15. [f] x,y lines poorly defined. [g] The spectrum of this representative complex has now been simulated by using the program EPR-SOF kindly supplied by Dr. J. R. Pilbrow. The best-fit parameters are very similar to those obtained by visual inspection; $g_\parallel = 1.971$, $g_\perp = 1.984$, $-A_\parallel = 144 \times 10^4$ cm^{-1}, $-A_\perp = 48 \times 10^4$ cm^{-1}, line widths $W_\parallel = 0.5$ mT, $W_\perp = 0.4$ mT. A small rhombicity in $g_\perp$ (±0.05%) and $A_\perp$ (±0.2%) also gave acceptable fits.

species such as $V^VL_2(OR)$ and $(V^VOL)_2O$.[9,31] The visible spectrum of **3** is notable for the presence of a strong charge-transfer band at 532 nm, which is a feature of non-oxo vanadium(IV) species.

Structure of 2a. The molecular structure and numbering scheme of $V^{IV}O$(tsalen) are shown in Figure 1. Bond lengths and bond angles are given in Tables IV and V. The molecule adopts the square-pyramidal geometry characteristic of oxovanadium(IV) chelates. Comparisons are made with appropriate bond lengths and angles in $V^{IV}O$(salen) and $[V^{IV}O(edt)_2]^{2-}$ in Table VI. The vanadyl V=O bond is shorter in **1** and **2a** than it is in $[V^{IV}O(edt)_2]^{2-}$. Possible reasons for the longer than usual bond in the last complex have been given by Christou et al.[14] Interestingly, the vanadium atom is also displaced slightly further out of the basal plane in the edt complex (0.668 Å) compared to the displacement for **1**[7] and **2a** (~0.608 Å). The average V-S bond lengths in **2a** and $[V^{IV}O(edt)_2]^{2-}$ are similar to each other and to those in the vanadium(III) μ-oxo dimer[12] $V_2O(SCH_2CH_2NMe_2)_4$. S-V-S angles in **2a** and $[V^{IV}O(edt)_2]^{2-}$ are similar in magnitude. The thiosalicylidene rings on each side of the basal plane are parallel and "stepped" in relation to each other.

ESR Spectra. A representative spectrum of complexes of type **2** is shown in Figure 2. The corresponding g and A values are given in Table VII together with those for $V^{IV}O$(salen),[7,32,33] $V^{IV}O(mquin)_2$,[34] and $[V^{IV}O(edt)_2]^{2-}$.[15] Complexes **2** all show similar spectral parameters, although **2b** displays slightly smaller $A_\parallel$ and $A_\perp$ values compared to the others. The $g_\parallel$ value for **2a** is larger than it is for the $VO(N_2O_2)$ analogues **1** and for the 2-methylquinolin-8-olate complex.[34] The $A_\parallel$ and $A_\perp$ values in the present complexes are slightly smaller than in the $VO(N_2O_2)$ compounds and slightly larger than in the $[VO(S)_4]^{2-}$ complex. The kinds of subtle changes observed between these in-plane chromophores N_2O_2, N_2S_2, and S_4 are rather similar to those noted recently for axial changes in VO(chel) and VS(chel) species (chel = salen^{2-}, acen^{2-}, $(edt)_2{}^{4-}$).[14,15,32] Unfortunately, the obscuring of d-d visible bands by charge-transfer bands in complexes **2** does not allow a more detailed analysis of g and A values in terms of molecular-orbital parameters.[15,32] Nevertheless, from a qualitative point of view, data of the type given in Table VII should prove useful for identifying donor atoms bonded to vanadyl groups in biological and crude oil systems. In the latter case the resolution so far obtained in the ESR spectra of oil fractions[11] is inferior to that in model systems.

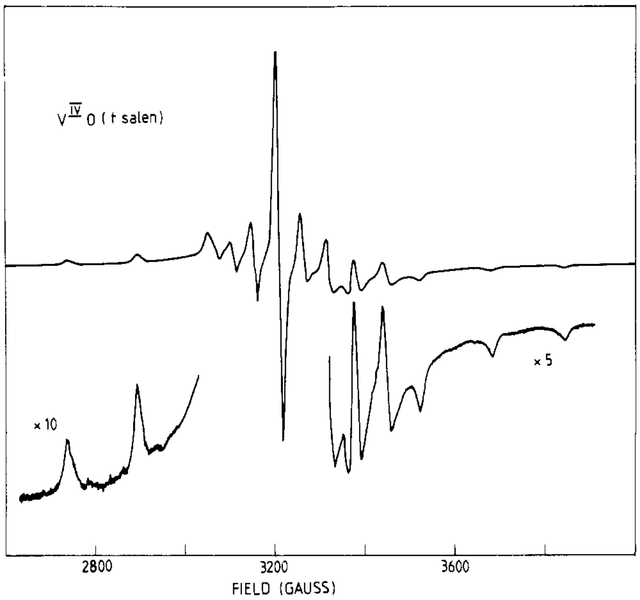

Figure 2. ESR spectrum of $V^{IV}O$(tsalen) (**2a**) in a frozen DMF glass at 110 K (microwave frequency 9.108 GHz).

Table VIII. Electrochemical Data[a]

complex	redox change	$E_{1/2}$,[b] V	ΔE_p,[c] mV	i_{pa}/i_{pc}
VO(tsalen) (**2a**)	VO^{3+}/VO^{2+}	+0.56	83	1.03
	VO^{2+}/V^{3+}	−1.29	77	0.80
VO(salen) (**1**)	VO^{3+}/VO^{2+}	+0.40	73	1.00
	VO^{2+}/V^{3+}	−1.58	irrev	
$[V(sal\text{-}NSO)_2]$ (**3**)	V^{4+}/V^{3+}	−0.24	68	1.00
	V^{3+}/V^{2+}	−1.57	82	1.00

[a] Conditions: Pt working and auxiliary electrodes; DMF solvent; SCE reference electrode; TBAP electrolyte. [b] $E_{1/2} = 0.5(E_{pc} - E_{pa})$ at scan rate 100 mV s^{-1}. [c] $\Delta E_p = E_{pc} - E_{pa}$ at scan rate 100 mV s^{-1}.

The ESR spectrum of the bis(tridentate), non-oxo complex **3** differs significantly from those of **2** especially with respect to the smaller $A_\parallel$ value and is very similar to that of a related $V^{IV}(ONO)_2$ complex of known trigonal-prismatic structure.[26,27] The x,y region of the spectrum of **3** was not sufficiently well-resolved to be able to detect anisotropy in the x and y parameters found to be necessary to fully interpret the $V^{IV}(ONO)_2$ spectrum.[27] The unpaired electron in **3** presumably occupies a predominantly d_{z^2} orbital, with small admixtures of $d_{x^2-y^2}$ and 4s orbitals, as in the $V^{IV}(ONO)_2$ complex[27] and in the $V(S)_6$ chromophore[35] of $[V(S_2C_2(CN)_2)_3]^{2-}$.

Electrochemistry. One of the aims of this study was to see how the redox properties of the oxovanadium(IV) complexes were affected by changing the in-plane ligand donors from O_2N_2 to S_2N_2. The results of cyclic voltammetry measurements are given in Table VIII for DMF solutions of the complexes $V^{IV}O$(tsalen) (**2a**), $V^{IV}O$(salen) (**1**), and $V^{IV}(sal\text{-}NSO)_2$ (**3**). Representative CV scans are shown in Figures 3 and 4. Complex **1** has been

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(31) Bosserman, P. J.; Sawyer, D. T. *Inorg. Chem.* **1982**, *21*, 1545.

(32) Callaghan, K. P.; Durand, P. J. *Inorg. Chem.* **1980**, *19*, 3211.

(33) Jezierski, A.; Raynor, J. B. *J. Chem. Soc., Dalton Trans.* **1981**, 1.

(34) (a) Collison, D.; Gahan, B.; Mabbs, F. E. *J. Chem. Soc., Dalton Trans.* **1987**, 111. (b) Stoklosa, H. J.; Wasson, J. R.; McCormick, B. J. *Inorg. Chem.* **1974**, *13*, 592.

(35) (a) Kwik, W.-L.; Stiefel, E. I. *Inorg. Chem.* **1973**, *12*, 2337. (b) Atherton, N. M.; Winscom, C. J. *Inorg. Chem.* **1973**, *12*, 383.

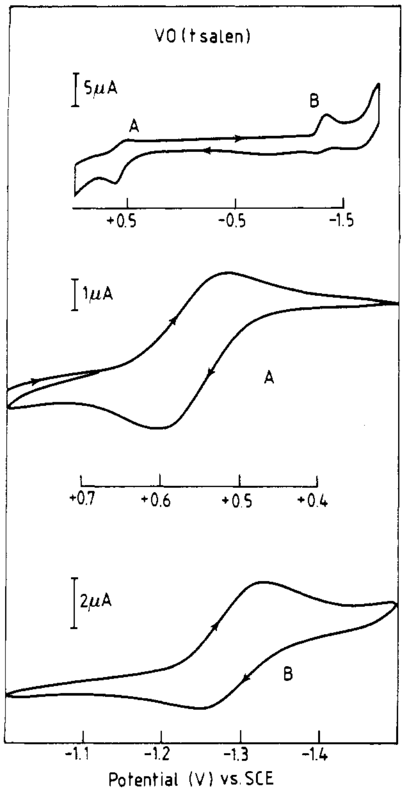

Figure 3. Cyclic voltammograms of $\mathrm{V^{IV}O(tsalen)}$ in DMF solution at 20 °C (scan speed 100 mV s^{-1}; reference electrode SCE).

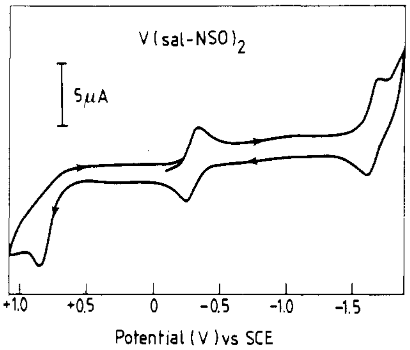

Figure 4. Cyclic voltammogram of $[\mathrm{V^{IV}(sal\text{-}NSO)_2}]$ (3) in DMF solution at 20 °C (scan speed 100 mV s^{-1}; reference electrode SCE).

studied previously in DMF,[2,6] MeCN,[7,8] and CH_2Cl_2,[36] and the present data are in good agreement with the previous results. **2a** shows two quasi-reversible waves at +0.56 and −1.29 V. Measurements on Zn(tsalen) in the range +1.5 to −2.5 V showed that, except for an irreversible anodic wave at ca. +1.0 V, there were no waves due to the ligand tsalen, and so the two waves observed for **2a** are metal-based. Variation of the scan rate between 100 and 500 mV s^{-1} showed only a marginal increase in ΔE_p for the +0.56 V wave and no increase for the −1.29 V wave. i_{pa}/i_{pc} for the latter wave was less than unity, which, together with the ΔE_p value of 77 mV, is indicative of a quasi-reversible process. The analogous wave for $\mathrm{V^{IV}O(salen)}$ shows no anodic component.[2,6,7]

The redox changes associated with these two waves are as given in Table VIII. It can be seen that it is easier to oxidize $\mathrm{V^{IV}O(salen)}$ to $[\mathrm{V^{V}O(salen)}]^+$ than it is to oxidize $\mathrm{V^{IV}O(tsalen)}$. Conversely, it is easier to reduce $\mathrm{V^{IV}O(tsalen)}$ to the $\mathrm{V^{III}}$ state. Such differences are generally compatible with the S_2N_2 donor set stabilizing the lower oxidation states. Unfortunately, $[\mathrm{VO(edt)_2}]^{2-}$ is reported to show electrochemically irreversible behavior with only a poorly defined anodic wave at ca. −0.43 V (SCE), and so the present $E_{1/2}$ "trends" can not be confirmed from these data.[14] However, a similar trend in the ease of reduction as a function of increasing S-donor was observed in the $\mathrm{V^{III}/V^{II}}$ couple of the series $\mathrm{V(acac)_3}$, $\mathrm{V(sacac)_3}$, $\mathrm{V(sacsac)_3}$.[37]

The bis(tridentate) complex **3** shows two near-reversible waves at −0.24 and −1.57 V, which can readily be assigned to the couples $[\mathrm{V^{IV}(sal\text{-}NSO)_2}]/[\mathrm{V^{III}(sal\text{-}NSO)_2}]^-$ and $[\mathrm{V^{III}(sal\text{-}NSO)_2}]^-/[\mathrm{V^{II}(sal\text{-}NSO)_2}]^{2-}$, respectively. An irreversible anodic wave at +1.0 V is probably due to ligand (or solvent) rather than $\mathrm{V^{V}/V^{IV}}$. The six-coordinate geometries favored by $\mathrm{V^{III}}$ and $\mathrm{V^{II}}$ are readily satisfied in this non-oxo vanadium(IV) complex, thus making one-electron-reduction processes facile. Similarly reversible processes have been observed for other non-oxo complexes.[2,6,8,28,31,38,39]

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Registry No. **1**, 36913-44-7; **1**$^+$, 100216-76-0; **2a**, 111349-11-2; **2a**$^+$, 111349-16-7; **2b**, 111349-12-3; **2c**, 111349-13-4; **2d**, 111349-14-5; **3**, 111349-15-6; **3**$^-$, 111349-17-8; **3**$^{2-}$, 111349-18-9; $\mathrm{V(salen)^+}$, 36670-35-6; $\mathrm{V(tsalen)^+}$, 111349-21-4; $[\mathrm{V(dmso)_6}](\mathrm{BF_4})_3$, 111349-19-0; $\mathrm{VO(acac)_2}$, 3153-26-2; $[\mathrm{VO(SCH_2CH_2S)_2}]^{2-}$, 89061-82-5; 2-mercaptobenzaldehyde, 29199-11-9; ethylenediamine, 107-15-3; 1,3-diaminopropane, 109-76-2; *o*-phenylenediamine, 95-54-5; 4,5-dimethyl-*o*-phenylenediamine, 3171-45-7.

Supplementary Material Available: Tables S1 and S2, listing hydrogen atom positional coordinates, anisotropic thermal parameters, and all bond lengths and angles (4 pages); Table S3, listing observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(36) Seangprasertkij, R.; Riechel, T. L. *Inorg. Chem.* **1986**, *25*, 3121.

(37) Boyd, P. D. W.; Hope, J.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1986**, 887.

(38) Seangprasertkij, R.; Riechel, T. L. *Inorg. Chem.* **1986**, *25*, 4268.

(39) Riechel, T. L.; de Hayes, L. J.; Sawyer, D. T. *Inorg. Chem.* **1976**, *15*, 1900.