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N,*N'*-Ethylenebis(salicylideniminato)oxovanadium(IV): A New Ligand Coordinating Sodium Cation in a Chain-Layered Structure. Synthesis and Crystal Structure

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Sodium cation is complexed by *N*,*N'*-ethylenebis(salicylideniminato)oxovanadium(IV), VO(salen), when a tetrahydrofuran or acetonitrile solution of NaBPh$_4$ is treated with VO(salen). This reaction affords [(VO(salen))$_2$Na]BPh$_4$, as a light green crystalline solid, which contains Na$^+$ trapped in a coordination cage provided by six oxygen atoms. The X-ray analysis performed on [(VO(salen))$_2$Na]BPh$_4$ shows that all the oxygens of VO(salen) are involved in coordination to the sodium cation, giving a cationic polymeric structure. The coordination geometry around Na$^+$ is pseudooctahedral, where the six oxygens are provided by four different VO(salen) units. Vanadium is five-coordinate in an approximate square-pyramidal environment. The vanadium atom is displaced by 0.606 Å above the least-squares plane of the four coordinating atoms of the salen unit, and the mean value of the V=O bond distance is 1.584 (2) Å. Crystallographic details for [(VO-(salen))$_2$Na]BPh$_4$: space group P$\bar{1}$ (triclinic), *a* = 16.053 (4) Å, *b* = 17.199 (4) Å, *c* = 11.221 (1) Å, α = 87.01 (2)°, β = 101.01 (2)°, γ = 124.29 (2)°, *V* = 2506.6 Å^3, *Z* = 2. The final *R* factor was 4.4% for 3161 observed reflections. It was found that the complexation of potassium cation by the same ligand occurs only in the presence of a catalytic amount of Na$^+$.

Introduction

A set of biocovalent oxygen atoms belonging to a transition-metal complex could be considered an "inorganic ligand". The appropriate geometrical arrangement of the oxygen atoms should generate, in some cases, "coordination traps" for alkali ions or other cationic species. The two oxygens in *N*,*N'*-ethylenebis(salicylideniminato)metal complexes, M(salen), have been recently found to coordinate several transition- and non-transition-metal ions, giving polynuclear compounds, in which the O,O rigid unit acts as a bidentate chelating ligand.[1-6]

M(salen)   *n* = 2, 3

M' = Na$^+$, NH$_4^+$, ...
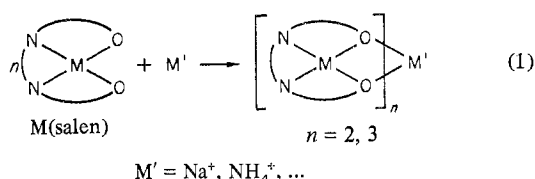
This reaction gives rise to polymetallic species, the utilization of which could be interesting in multicenter metal-promoted molecular activation processes.[7,8] M(salen) are not selective ligands, since they adapt themselves to various ionic dimensions,[4] so a strategy could be devised in finding selective ligands. Selective traps for alkali cations can be provided, for example, by increasing the number of the oxygen donor atoms arranged in a suitable geometry around the transition metal.

It is well-known that, in order to achieve high overall selectivity in the complexation of alkali cations by "crown" polyethers, the ligand should be as rigid as possible so as not to be able to adjust easily to smaller or larger cations, like the hydration shell, for instance.[9] The utilization of transition-metal complexes as ligands for alkali cations is mainly suggested by their rigid conformation. So they have the ability to discriminate against the cations which are either smaller or larger than the preferred ones.

We report here the complexation of sodium cation occurring with the tridentate "inorganic ligands", *N*,*N'*-ethylenebis-(salicylideniminato)oxovanadium(IV), VO(salen), and *N*,-
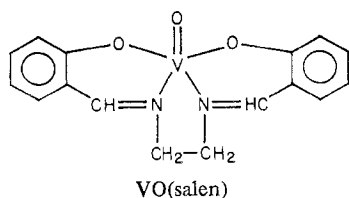
VO(salen)

N'-(*o*-phenylene)bis(salicylideniminato)oxovanadium(IV), VO(saloph), along with the X-ray structure analysis carried out on the polymeric sodium complex {[(VO(salen))$_2$Na]-BPh$_4$}$_n$. Moreover, it was found that the complexation of potassium cation by the same ligands occurs only in the presence of a catalytic amount of NaBPh$_4$.

Experimental Section

Reactions have been carried out in the air. *N*,*N'*-Ethylenebis-(salicylideniminato)oxovanadium(IV) (VO(salen)), and *N*,*N'*-(*o*-phenylene)bis(salicylideniminato)oxovanadium(IV) were prepared by using the usual previously described procedure.[10] The IR spectra were recored on a Perkin-Elmer 337 spectrometer.

Preparations. Reaction of *N*,*N'*-Ethylenebis(salicylideniminato)-oxovanadium(IV) with Sodium Tetraphenylborate. *N*,*N'*-Ethylene-bis(salicylideniminato)oxovanadium(IV), VO(salen) (0.5 g, 1.50 mmol), was added to an acetonitrile (25 mL) solution of NaBPh$_4$ (0.6 g, 1.75 mmol). The suspension is vigorously stirred for 30 s and then filtered. A light green solid immediately crystallized out from the solution (ca. 50%). Then the solid was gently dried in vacuo. Anal. Calcd for [(VO(salen))$_2$Na]BPh$_4$ (C$_{56}$H$_{48}$BN$_4$NaO$_6$V$_2$): C, 66.66; H, 4.76; N, 5.55; V, 10.12; Na, 2.28. Found: C, 66.62; H, 4.93; N, 5.69; V, 10.35; Na, 2.14.

This procedure may be applied wherever a nice crystalline solid is required. By use of a higher Na/V molar ratio and the avoidance of filtration, VO(salen) can be converted quantitatively into [(VO-(salen))$_2$Na]BPh$_4$ as microcrystalline powdered solid. The IR spectrum (Nujol) of the solid did not show the presence of MeCN. Similar procedure was applied for the reaction between *N*,*N'*-(*o*-phenylene)bis(salicylideniminato)oxovanadium(IV), VO(saloph) (0.6

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Table I. Summary of Crystal Data

mol formula	C$_{56}$H$_{48}$N$_4$O$_6$V$_2$BNa
mol wt	1008.7
cryst shape and size	irregular elengated shape with 8 faces: 2$\bar{1}$0, $\bar{1}$10, $\bar{2}$10, 1$\bar{1}$0, $\bar{1}$04, $\bar{1}$45, 1$\bar{3}$5, 24$\bar{5}$; approximate dimensions 0.1 × 0.04 × 0.3 mm
space group	P$\bar{1}$
unit cell parameters, A or deg	a = 16.053 (4), α = 87.01 (2)
	b = 17.199 (4), β = 101.01 (2)
	c = 11.221 (1), γ = 124.29 (2)
unit cell vol, A^3	2506.6
density (calcd), g/cm^3	1.336
density (flotation), g/cm^3	1.34 (1)
radiation used in data collection	Cu Kα (λ = 1.541 78 A)
linear abs coeff, μ, cm^{-1}	36.7

g, 1.57 mmol), and NaBPh$_4$ (0.7 g, 2.04 mmol), carried out in THF (50 mL) (yield ca. 50%). Anal. Calcd for C$_{64}$H$_{48}$BN$_4$NaO$_6$V$_2$: C, 69.56; H, 4.34; N, 5.07; V, 9.23; Na, 2.08. Found: C, 69.38; H, 4.26; N, 5.28; V, 9.04; Na, 2.13. IR spectra show the presence of the BPh$_4^-$ unit displaying broad strong bands in the 750–700-cm^{-1} region. The V=O stretching vibration was found as a broad band at 960 cm^{-1} in [(VO(salen))$_2$Na]BPh$_4$ and at 970 cm^{-1} in [(VO(saloph))$_2$Na]BPh$_4$. Stretching vibrations fall at 980 and 990 cm^{-1} in free VO(salen) and VO(saloph), respectively.

Potassium Complexation. Three typical experiments are reported in order to prove the influence of Na$^+$ on the K$^+$ complexation by VO(salen): (a) VO(salen) (0.5 g, 1.50 mmol) suspended in a solution of KBPh$_4$ (1.0 g, 2.65 mmol) in acetonitrile (20 mL) is stirred for 4 days. The solid, filtered off and washed with acetonitrile, does not contain K$^+$ as checked by the atomic absorption analysis, and it was identified as VO(salen) by IR spectrum. (b) NaBPh$_4$ (0.50 g, 1.46 mmol) and KBPh$_4$ (0.5 g, 1.40 mmol) were dissolved in acetonitrile (40 mL) and then VO(salen) (0.51 g, 1.53 mmol) was added. The suspension was stirred for 4 days. The solid, filtered off and washed, contains Na = 2.02% and K = 0.218%. (c) KBPh$_4$ (0.4 g, 1.12 mmol) and NaBPh$_4$ (0.002 g) were dissolved in acetonitrile (20 mL). VO-(salen) (0.4 g, 1.20 mmol) was added as solid and the resulting suspension stirred for 4 days. The solid contains 0.55% K$^+$.

X-ray Analysis. The crystals selected for X-ray analysis were sealed in glass capillaries. Weissenberg photographs showed triclinic symmetry; the P$\bar{1}$ space group was chosen and subsequently confirmed by the successful refinement of the crystal structure. Refined cell dimensions were obtained by a least-squares fit of the setting angles of 26 reflections, carefully measured on the diffractometer. Crystal data are listed in Table I.

Data Collection. Intensities were collected from a crystal of approximate dimensions 0.1 × 0.04 × 0.3 mm, mounted with the c axis parallel to the spindle axis of an on-line Siemens AED diffractometer, using Cu Kα radiation. θ–2θ scan method and "five-points" technique[11] were used.

A total of 6282 independent reflections were measured, of which 3161, obeying the relation $I > 4\sigma(I)$, where [$\sigma^2(I)$ = total counts + + (0.005I)^2], were used for the structure determination. The intensity of a selected standard reflection, measured every 15 reflections, fluctuated within ±1.5% during the experiment; the scale factor was adjusted on the assumption that all the other intensities varied at the same rate. Intensities were corrected for Lorentz and polarization effects and converted to F^2. The absorption correction was applied;[12] the transmission factors ranged from 0.45 to 0.78.

Structure Determination and Refinement. The structure was solved by using Patterson and Fourier methods. Block-matrix least-squares refinements on F were performed in which the function minimized was $\sum w(F_o - F_c)^2$; Cruickshank's weighting scheme[13] was used. Neutral atomic scattering factors were from Cromer and Mann[14] for nonhydrogen atoms and from Stewart et al.[15] for hydrogen.
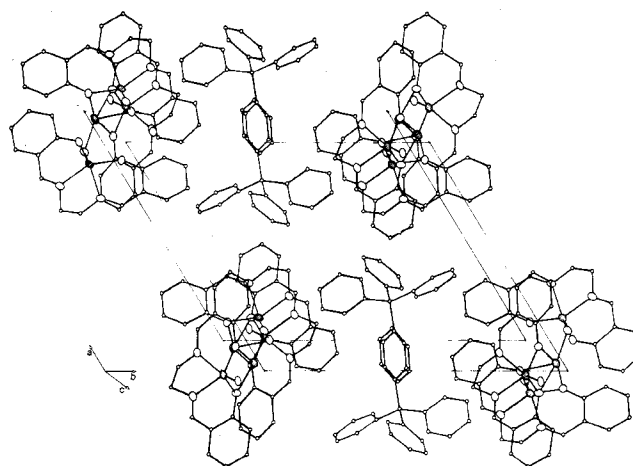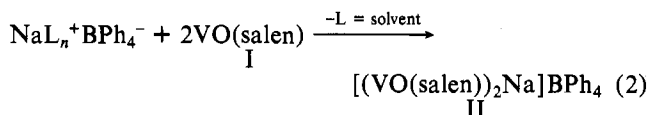

Figure 1. Crystal packing of {[(VO(salen))$_2$Na]BPh$_4$}$_n$ viewed nearly along the c direction.

Anomalous dispersion corrections were applied to the scattering factor of V[16]. With the exception of ORTEP,[17] all the computer programs were written by Immirzi.[18] The positions of the two independent V atoms were derived from the Patterson map. Subsequent electron density maps revealed the positions of the other nonhydrogen atoms. The coordinates of the hydrogen atoms were calculated according to the usual sp^2 or sp^3 geometry; in many cases, these calculated positions could be verified by the difference electron density distribution. The positional and isotropic thermal parameters of the hydrogen atoms were varied in additional cycles of the refinement. The final unweighted R factor was 0.044. Positional and anisotropic thermal parameters from the final least-squares cycle are reported in Table II.

Results and Discussion

N,N'-Ethylenebis(salicylideniminato)oxovanadium(IV), VO(salen) (I), is only slightly soluble in tetrahydrofuran (THF), acetone, and acetonitrile. However, upon addition of VO(salen) to NaBPh$_4$ in these solvents, a green solution is produced, from which the sodium cation complex II crystallizes out as a light green solid, stable in air. Identical results were

$$\text{NaL}_n^+\text{BPh}_4^- + 2\text{VO(salen)} \xrightarrow{\quad -\text{L = solvent}\quad}$$
$$\text{I}$$

$$[(\text{VO(salen)})_2\text{Na}]\text{BPh}_4 \quad (2)$$
$$\text{II}$$

obtained by using N,N'-(o-phenylene)bis(salicylideniminato)oxovanadium(IV), VO(salen) (III), which gives [(VO(saloph))$_2$Na]BPh$_4$ (IV). Although no particular care was taken in avoiding the presence of water in the solvent, nevertheless we never observed the presence of water in II or IV. The choice of sodium tetraphenylborate as sodium salt was suggested by its high solubility in the organic solvents used and because it contains a noncoordinating anion for alkali cations. II and IV were characterized from analytical and IR determinations. II and IV do not contain molecules of solvent. The IR spectrum shows the presence of the BPh$_4^-$ bands in the 700–750-cm^{-1} region. A slight change in the V=O stretching vibration, which appears as a broad band lowered to 960 cm^{-1} ($\Delta\nu$ ca. 20 cm^{-1}) in II and to 970 cm^{-1} ($\Delta\nu$ ca. 20 cm^{-1}) in IV, suggests that this oxygen atom could be involved in the complexation of sodium cation. Rather poor information, however, can be derived from these measurements concerning the solid-state nature of complexes like II, which was examined by X-ray analysis.

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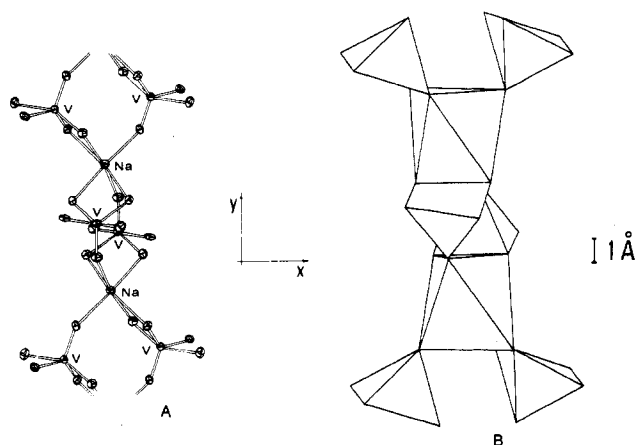
Figure 2. Two representations of the coordination polyhedra around vanadium and sodium along the chain of complex II, $\{[(VO(salen))_2Na]^+\}_n$.

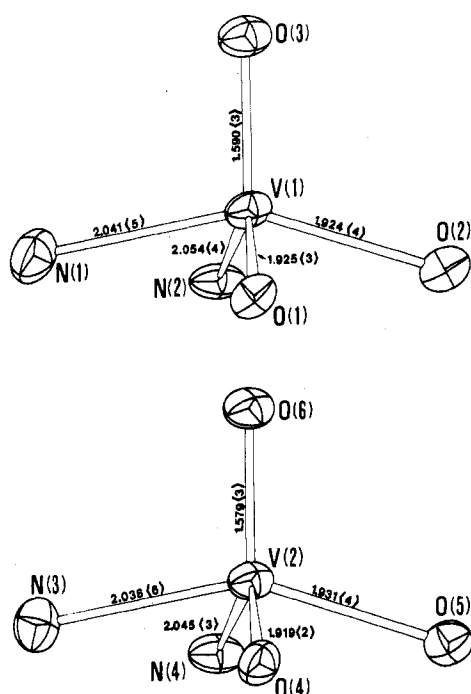**Figure 3.** ORTEP drawing of the coordination polyhedra around V(1) and V(2).
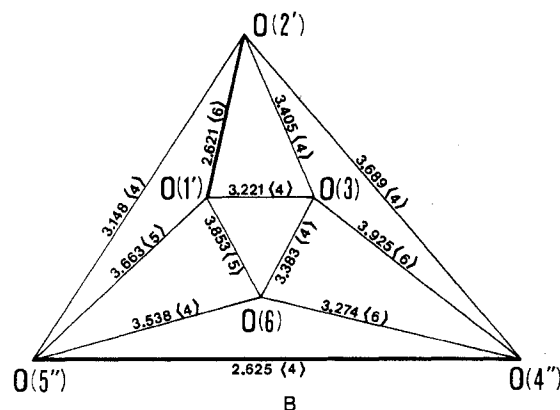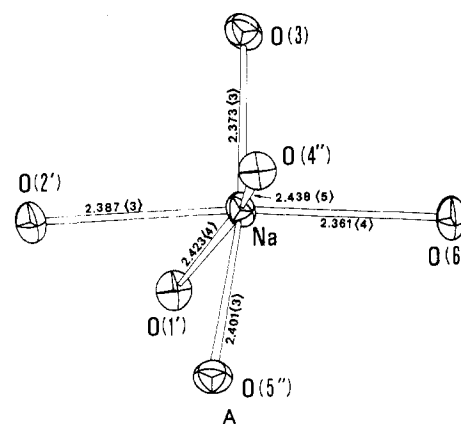

Figure 4. (A) An ORTEP drawing of sodium coordination polyhedron: single prime = $-x, -y, 1-z$; double prime = $-x, -y, -z$. (B) A Schlegel projection of sodium coordination polyhedron.

Description of the Structure of $[(VO(salen))_2Na]BPh_4$ (II). The structure of II consists of parallel cationic chains, growing along the c direction of the crystal and kept apart by the itnerposed BPh_4^- anions (Figure 1). The framework of each chain is formed by the oxygen and nitrogen atoms of the VO(salen) units which are arranged alternately two by two in such a way to coordinate a Na^+ ion in pseudooctahedral cavities provided by six oxygen atoms of four different VO(salen) units. Figure 2 shows two different sketches of the same piece of the chain, displaying in (A) the coordination bonds and showing in (B) the coordination polyhedra.

(a) Coordination Polyhedron of Vanadium. The structure contains two crystallographically nonequivalent VO(salen). The coordination geometry around the two vanadium atoms is shown in Figure 3, together with the numbering scheme for the donor atoms and the related bond distances; the bond angles are given in Table III. If we choose the apex-to-base angles as a diagnostic[10,19] for the coordination geometry, we

observe (see Table III) that the single values of the vanadyl oxygen–V–basal ligand angles fall in the range $\geq 90°$ and $\leq 115°$, indicating the angular distortions from a trigonal bipyramid to be much greater than those from a square pyramid. This is further confirmed by an inspection on the dihedral angles chosen by Muetterties et al.[20] for describing intermediate structures between limiting trigonal bipyrimdal and square pyramid polyhedra. Table IV lists the ideal and observed dihedral angles for the coordination polyhedra around V(1) and V(2) following the notation given in ref 20. The base of this square pyramid is formed by two oxygen and two nitrogen atoms of the salen unit with mean V–O and V–N bond distances of 1.925 (2) and 2.004 (2) Å,[21] respectively. An apical vanadyl oxygen completes the square pyramid with a mean V–O distance of 1.584 (2) Å, a value which is within the range 1.56–1.67 Å reported for other vanadyl complexes.[10] The vanadium atom is displaced 0.606 (2) Å above the least-squares plane of the four coordinating atoms of the salen ligand. A similar geometry has been observed in other oxo-vanadium complexes.[22,23] Bond distances within the salen do not differ significantly from those previously reported for many salen complexes.[24]

(b) Coordination Polyhedron of Sodium Cation. The six oxygen donor atoms are arranged around Na^+ so as to confer to the coordination polyhedron an approximate C_2 symmetry.

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**Table II.** Final Atomic Positional and Anisotropic Thermal Parameters (B_{ij}'s) for Nonhydrogen Atoms in [(VO(salen))$_2$Na] BPh$_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
V(1)	15810 (6)	13240 (5)	55350 (7)	2.92 (3)	2.40 (3)	2.24 (3)	1.35 (5)	1.52 (5)	0.40 (5)
V(2)	1990 (6)	14330 (5)	−2300 (7)	3.86 (4)	2.19 (3)	2.54 (3)	3.31 (6)	1.41 (6)	0.66 (5)
Na	110 (12)	−160 (11)	24840 (14)	3.27 (8)	2.51 (7)	2.22 (7)	2.49 (12)	1.77 (12)	0.51 (11)
O(1)	1251 (2)	223 (2)	6410 (3)	4.07 (15)	3.38 (14)	3.25 (14)	4.53 (25)	2.59 (24)	0.75 (22)
O(2)	512 (2)	1260 (2)	6167 (3)	4.41 (16)	2.55 (13)	3.29 (14)	3.84 (24)	2.57 (24)	1.11 (21)
O(3)	1224 (2)	1123 (2)	4098 (3)	3.66 (15)	2.93 (13)	2.84 (14)	1.79 (24)	0.94 (23)	−0.57 (21)
O(4)	−899 (2)	373 (2)	−1306 (3)	3.80 (15)	3.34 (14)	3.20 (14)	4.35 (24)	2.12 (24)	0.32 (22)
O(5)	1111 (2)	1314 (2)	−984 (3)	3.08 (14)	3.32 (14)	3.06 (14)	2.78 (24)	0.42 (22)	−0.61 (22)
O(6)	317 (2)	1179 (2)	1137 (3)	5.49 (18)	2.61 (13)	3.33 (14)	4.89 (26)	2.62 (26)	1.90 (22)
N(1)	3035 (3)	1642 (3)	5749 (4)	3.9 (2)	4.5 (2)	4.7 (2)	3.9 (3)	3.6 (3)	0.5 (3)
N(2)	2457 (3)	2757 (2)	5931 (3)	3.87 (19)	2.82 (16)	1.94 (16)	1.22 (29)	1.06 (28)	1.02 (26)
N(3)	−761 (3)	1856 (3)	−248 (4)	4.5 (2)	3.1 (2)	4.8 (2)	4.5 (3)	1.9 (3)	−0.3 (3)
N(4)	1156 (3)	2862 (3)	−310 (3)	4.8 (2)	2.3 (2)	2.6 (2)	2.9 (3)	0.9 (3)	0.9 (3)
C(1)	1658 (4)	−262 (3)	6516 (4)	4.9 (3)	4.4 (2)	3.9 (2)	5.8 (4)	1.7 (4)	−0.7 (4)
C(2)	1098 (5)	−1183 (4)	6840 (5)	7.5 (3)	4.4 (3)	7.3 (3)	9.4 (5)	6.5 (6)	3.1 (5)
C(3)	1472 (6)	−1713 (5)	6956 (7)	10.0 (5)	6.1 (3)	9.7 (5)	10.7 (7)	7.2 (8)	5.7 (7)
C(4)	2464 (7)	−1341 (6)	6779 (10)	13.4 (7)	10.5 (6)	18.6 (9)	20.8 (11)	9.7 (13)	3.6 (11)
C(5)	3039 (6)	−432 (6)	6486 (10)	8.0 (5)	9.3 (5)	18.7 (8)	12.8 (8)	8.0 (10)	4.6 (10)
C(6)	2673 (5)	145 (4)	6320 (6)	5.3 (3)	5.8 (3)	8.5 (4)	7.8 (5)	1.7 (6)	−0.9 (6)
C(7)	3314 (4)	1090 (4)	6014 (6)	3.8 (3)	5.6 (3)	8.3 (4)	3.6 (5)	1.6 (5)	−2.4 (5)
C(8)	3751 (4)	2603 (4)	5405 (5)	3.3 (3)	6.3 (3)	5.9 (3)	0.5 (5)	3.6 (5)	3.4 (5)
C(9)	3564 (4)	3245 (4)	5974 (5)	4.3 (3)	4.2 (3)	5.4 (3)	−0.3 (4)	1.3 (5)	−0.2 (5)
C(10)	2124 (4)	3240 (3)	6164 (4)	7.3 (3)	2.3 (2)	2.7 (2)	3.9 (4)	1.0 (4)	1.4 (3)
C(11)	1078 (4)	2887 (3)	6252 (4)	6.7 (3)	2.8 (2)	3.2 (2)	5.7 (4)	2.2 (4)	0.7 (3)
C(12)	833 (5)	3537 (4)	6367 (5)	10.8 (4)	4.2 (3)	2.9 (2)	9.4 (6)	1.7 (5)	1.5 (4)
C(13)	−120 (6)	3254 (4)	6475 (5)	13.5 (5)	6.8 (3)	4.0 (3)	15.7 (8)	3.6 (6)	1.1 (5)
C(14)	−865 (5)	2312 (5)	6453 (5)	9.4 (4)	8.4 (4)	4.8 (3)	14.7 (7)	3.8 (6)	2.7 (5)
C(15)	−658 (4)	1642 (4)	6357 (5)	6.2 (3)	5.8 (3)	3.4 (2)	7.8 (5)	2.4 (4)	2.0 (4)
C(16)	330 (4)	1904 (3)	6251 (4)	6.3 (3)	3.3 (2)	2.2 (2)	6.4 (4)	2.4 (4)	1.6 (3)
C(17)	−1902 (3)	−31 (3)	−1514 (4)	3.5 (2)	2.9 (2)	3.4 (2)	2.8 (4)	1.8 (4)	0.6 (3)
C(18)	−2544 (4)	−915 (4)	−2118 (5)	2.9 (2)	3.8 (2)	5.9 (3)	2.7 (4)	3.0 (4)	−0.4 (4)
C(19)	−3588 (4)	−1374 (4)	−2350 (6)	3.6 (3)	4.2 (3)	8.7 (4)	2.0 (4)	2.2 (5)	−2.9 (5)
C(20)	−4035 (5)	−966 (5)	−2006 (8)	3.8 (3)	6.6 (4)	12.9 (6)	4.3 (6)	1.7 (7)	−4.3 (8)
C(21)	−3430 (5)	−82 (5)	−1405 (7)	5.0 (3)	7.2 (4)	12.2 (5)	8.0 (6)	2.0 (7)	−2.6 (7)
C(22)	−2349 (4)	411 (3)	−1165 (5)	4.1 (3)	3.9 (2)	6.4 (3)	5.2 (4)	3.4 (5)	2.0 (4)
C(23)	−1735 (4)	1346 (4)	−601 (5)	5.9 (3)	4.1 (2)	6.8 (3)	7.2 (5)	2.6 (5)	−0.3 (4)
C(24)	−216 (5)	2810 (4)	317 (5)	7.6 (3)	4.0 (2)	5.2 (3)	7.7 (5)	1.9 (5)	−0.9 (4)
C(25)	735 (4)	3418 (3)	−207 (5)	6.6 (3)	2.2 (2)	4.8 (3)	4.9 (4)	−1.6 (5)	−0.7 (4)
C(26)	2097 (4)	3308 (3)	−436 (4)	5.7 (3)	2.5 (2)	2.5 (2)	1.3 (4)	−0.1 (4)	0.7 (3)
C(27)	2645 (4)	2901 (3)	−610 (4)	3.1 (2)	4.3 (2)	3.2 (2)	1.6 (4)	1.3 (4)	0.6 (4)
C(28)	3709 (4)	3487 (4)	−504 (5)	4.8 (3)	5.0 (3)	4.1 (3)	0.2 (5)	0.8 (5)	−2.3 (4)
C(29)	4268 (4)	3151 (5)	−614 (6)	4.0 (3)	8.7 (4)	5.1 (3)	1.9 (6)	2.1 (5)	−1.8 (6)
C(30)	3780 (4)	2190 (5)	−869 (5)	4.9 (3)	10.5 (4)	3.8 (3)	9.7 (6)	1.7 (5)	−1.0 (5)
C(31)	2716 (4)	1578 (4)	−993 (5)	3.7 (3)	6.2 (3)	3.7 (3)	4.5 (5)	0.4 (4)	−0.6 (4)
C(32)	2125 (4)	1918 (3)	−840 (4)	3.9 (2)	4.4 (2)	2.6 (2)	3.4 (4)	1.2 (4)	−0.1 (4)
C(33)	3067 (3)	6063 (3)	4656 (4)	2.0 (2)	2.7 (2)	4.0 (2)	2.2 (3)	1.3 (3)	0.9 (3)
C(34)	2862 (4)	6576 (4)	5335 (5)	4.0 (3)	5.0 (3)	4.9 (3)	6.3 (4)	0.3 (4)	−1.2 (4)
C(35)	3232 (4)	6812 (4)	6570 (5)	5.6 (3)	5.4 (3)	5.2 (3)	6.3 (5)	2.0 (5)	−1.8 (5)
C(36)	3830 (4)	6538 (4)	7193 (5)	4.3 (3)	4.8 (3)	3.9 (3)	2.8 (4)	0.0 (4)	−2.2 (4)
C(37)	4059 (4)	6038 (4)	6583 (5)	3.3 (2)	4.6 (2)	5.3 (3)	4.4 (4)	−0.4 (4)	0.8 (4)
C(38)	3691 (3)	5807 (3)	5347 (4)	3.1 (2)	2.9 (2)	4.2 (2)	2.9 (4)	1.5 (4)	0.3 (3)
C(39)	2777 (3)	4969 (3)	2835 (4)	3.0 (2)	3.2 (2)	2.6 (2)	3.8 (3)	0.7 (3)	0.3 (3)
C(40)	3688 (4)	5216 (3)	2488 (4)	3.3 (2)	3.2 (2)	4.6 (3)	3.7 (4)	1.5 (4)	0.1 (4)
C(41)	3913 (4)	4587 (4)	2308 (5)	4.4 (3)	5.4 (3)	4.7 (3)	6.7 (5)	1.9 (4)	−0.2 (4)
C(42)	3232 (4)	3646 (4)	2450 (5)	5.9 (3)	6.5 (3)	3.6 (3)	9.7 (5)	0.2 (4)	−0.5 (4)
C(43)	2323 (4)	3358 (4)	2789 (4)	5.4 (3)	1.9 (2)	3.5 (2)	2.7 (4)	0.1 (4)	0.6 (3)
C(44)	2111 (3)	4013 (3)	2968 (4)	3.3 (2)	3.4 (2)	3.3 (2)	3.8 (4)	0.4 (4)	0.6 (3)
C(45)	1359 (3)	5314 (3)	2898 (4)	3.2 (2)	3.1 (2)	3.7 (2)	4.0 (4)	2.1 (3)	−0.0 (3)
C(46)	828 (3)	5373 (3)	1799 (4)	3.5 (2)	4.2 (2)	3.3 (2)	4.8 (4)	2.0 (4)	1.0 (4)
C(47)	−235 (4)	4903 (4)	1541 (4)	4.2 (3)	5.5 (3)	3.4 (2)	6.7 (5)	−0.5 (4)	−0.3 (4)
C(48)	−808 (3)	4372 (3)	2398 (5)	2.2 (2)	4.4 (2)	5.4 (3)	2.6 (4)	−0.2 (4)	−1.5 (4)
C(49)	−315 (4)	4326 (4)	3486 (5)	3.4 (2)	5.3 (3)	5.0 (3)	3.8 (4)	3.5 (4)	2.5 (4)
C(50)	736 (4)	4778 (3)	3736 (4)	3.4 (2)	4.8 (3)	4.1 (2)	4.4 (4)	1.2 (4)	2.5 (4)
C(51)	3182 (3)	6697 (3)	2376 (4)	2.6 (2)	3.1 (2)	4.7 (3)	3.0 (4)	0.9 (4)	1.0 (4)
C(52)	3708 (4)	7625 (4)	2846 (5)	5.7 (3)	4.1 (3)	5.2 (3)	5.7 (5)	−0.1 (5)	1.2 (4)
C(53)	4147 (5)	8385 (4)	2104 (6)	6.1 (3)	3.3 (3)	9.3 (4)	4.0 (5)	0.8 (6)	2.5 (5)
C(54)	4046 (5)	8239 (4)	901 (6)	5.9 (3)	5.9 (3)	9.8 (4)	7.4 (6)	7.4 (6)	8.7 (6)
C(55)	3519 (5)	7330 (4)	400 (6)	5.8 (3)	7.3 (4)	7.7 (4)	9.2 (6)	5.5 (6)	4.9 (6)
C(56)	3110 (4)	6584 (3)	1122 (5)	6.1 (3)	3.8 (2)	5.0 (3)	5.4 (5)	5.2 (5)	3.3 (4)
B	2598 (4)	5768 (4)	3180 (5)	2.7 (2)	3.8 (3)	4.2 (3)	3.7 (4)	2.5 (4)	1.6 (4)

[a] The form of the expression for the anisotropic temperature factors is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

Table III. Sodium and Vanadium Inner-Coordination-Sphere Bond Angles (Deg)

Sodium Cation[a]

O(3)-Na-O(6)	91.2 (1)	O(6)-Na-O(4')	86.0 (2)
O(3)-Na-O(1')	84.3 (1)	O(6)-Na-O(5')	96.0 (1)
O(3)-Na-O(4')	109.3 (1)	O(1')-Na-O(2')	66.0 (1)
O(3)-Na-O(5')	170.8 (2)	O(1')-Na-O(4')	161.0 (1)
O(6)-Na-O(1')	107.3 (2)	O(1')-Na-O(5')	98.8 (1)
O(6)-Na-O(2')	172.6 (2)	O(2')-Na-O(4')	99.7 (2)
		O(2')-Na-O(5')	82.2 (1)
		O(4')-Na-O(5')	65.7 (1)

Vanadium

O(1)-V(1)-O(2)	85.8 (2)	O(4)-V(2)-O(5)	86.0 (7)
O(1)-V(1)-O(3)	114.2 (1)	O(4)-V(2)-O(6)	113.1 (1)
O(1)-V(1)-N(1)	87.0 (2)	O(4)-V(2)-N(3)	87.8 (2)
O(1)-V(1)-N(2)	136.7 (1)	O(4)-V(2)-N(4)	137.3 (1)
O(2)-V(1)-O(3)	108.0 (2)	O(5)-V(2)-O(6)	108.1 (1)
O(2)-V(1)-N(1)	151.2 (2)	O(5)-V(2)-N(3)	150.9 (2)
O(2)-V(2)-N(2)	87.9 (2)	O(5)-V(2)-N(4)	88.0 (2)
O(3)-V(1)-N(1)	100.4 (2)	O(6)-V(2)-N(3)	100.5 (2)
O(3)-V(1)-N(2)	108.5 (2)	O(6)-V(2)-N(4)	109.0 (1)
N(1)-V(1)-N(2)	78.4 (2)	N(3)-V(2)-N(4)	77.5 (2)

[a] Single prime $= -x, -y, 1 - z$. Double prime $= -x, -y, -z$.

Table IV. Ideal and Observed Angles for the Two Polyhedra around V(1) and V(2)
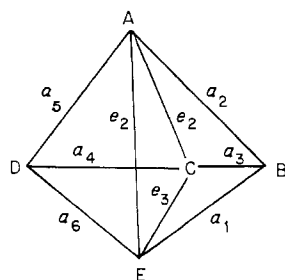
	(e_1, e_2, e_3)	$(a_1, a_2, \delta \cdots, a_6)$
tbp[a]	53.1, 53.1, 53.1	101.5, 101.5, 101.5, 101.5, 101.5, 101.5
sqp[b]	75.7, 75.7, 0.0	119.8, 75.7, 119.8, 119.8, 75.7, 119.8
V(1)[c]	68, 68, 14	116, 81, 117, 115, 81, 117
V(2)[d]	69, 67, 13	117, 81, 119, 115, 80, 118

[a] tbp = trigonal bipyramid. [b] sqp = square pyramid. [c] A = O(3), B = O(2), C = O(1), D = N(1), E = N(2) around V(1). [d] A = O(6), B = O(5), C = O(4), D = N(3), E = N(4) around V(2).

A perspective view of the polyhedron as well as a Schlegel projection are shown in Figure 4 (A and B). The main distortion from a regular octahedron is due to the short distance (average 2.623 (3) Å) of the O–O bites of the two salen ligands,[4,25] all the other O–O distances (see Figure 4B) ranging from 3.15 to 3.93 Å. The O–O bites, which correspond to edges shared by two polyhedra, impose a mean O–Na–O bond angle of 65.8 (2)° with a mean Na–O interionic distance of 2.405 (1) Å, significantly greater than that involving the vanadyl oxygen, average 2.368 (2) Å. The last value is very close to the sum of the ionic radii, 2.34 Å. A quite similar geometry has been observed for [(Co(salen))$_2$Na(THF)$_2$]BPh$_4$.[25] The magnitude of the O–O bite compares also very well with those found for N,N'-ethylenebis(acetylacetoniminato)oxovanadium(IV) (2.67 Å),[22] and bis(acetylacetonato)oxovanadium(IV) (2.61 Å).[26] The unchanged O–O distance with respect to the free O–O bite depends on the rigid conformation of the ligands imposing on the vanadium an unchangeable

coordination geometry. Furthermore, no significant variation of the V—O and V=O bond lengths is observed if they are compared with the value found for other vanadyl chelates.[27] It has been already noticed that when the oxygen atom of the M(salen) molecule is coordinated to the metal atom of another M(salen) unit to give a dimeric species (M(salen))$_2$ or when it is involved in hydrogen bonds, a significant lengthening of the corresponding M–O distance is observed.[24] Since no lengthening is observed upon coordination to Na$^+$, it may be thought that an essentially ionic interaction between oxygen and Na$^+$ does not influence the charge distribution in the V–O bonds.

Oxovanadium chelate complexes have been recently employed as ligands for synthesizing polynuclear species. In these complexes, however, only the ligand oxygens are involved in bridging two metal centers.[28] The vanadyl oxygen does not participate in bonding another metal center. A few years ago, it was supposed that the vanadyl oxygen bridged two metal centers in a binuclear Ru—O=V unit.[29]

The tetraphenylborate ion structural parameters are in good agreement with those recently reported. The mean B–C bond lengths average out at 1.64 (1) Å, whereas the mean value of the C–C distances of the phenyl rings is 1.40 (1) Å. The angles of the four phenyl groups exhibit the same trend as already observed.[4,25]

Potassium Complexation. When reaction 2 is carried out in the presence of KBPh$_4$ instead of NaBPh$_4$, the complexation of K$^+$ does not occur. However, when an acetonitrile solution containing both NaBPh$_4$ and KBPh$_4$ is reacted with VO(salen), a microcrystalline solid was obtained containing both sodium and potassium cations. Complexation of K$^+$ occurs with a rather high K$^+$/Na$^+$ molar ratio or even in the presence of a catalytic amount of Na$^+$. Therefore it seems that Na$^+$ promotes the potassium cation complexation, which does not occur in its absence. This finding is reminiscent of the complexation of alkali cations by means of zirconium–phosphate systems.[30] The complexation of potassium cation by these systems requires the previous complexation of sodium cation, which is subsequently exchanged by the incoming K$^+$ cation. It is rather difficult to suggest the same mechanism in our case, since this would imply the formation of the polymeric sodium complex in a first step, which is followed by a Na–K exchange occurring mainly on the insoluble solid. A more plausible hypothesis would suggest an exchange process in an earlier step in solution occurring when the coordination cage of the sodium cation is provided partially by the oxygen atoms of the oxovanadium complex and by the solvent molecules.

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