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Selenium Oxychloride as an Effective Chlorinating Agent and Solvent for Vanadium(IV) Complexes. An ESR Study

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The $VCl_2(chel)_2$ complexes were obtained previously by direct reaction of VCl_4 and chelating ligands [1], and by chlorination of $VO(chel)_2$ by $SOCl_2$ [2–4] and PCl_5 [3]. In this paper the effective chlorination of oxovanadium(IV) dimeric and monomeric complexes by $SeOCl_2$ and the properties of $SeOCl_2$ as a solvent for the dichlorovanadium(IV) complexes are discussed.

Experimental

Selenium oxychloride reacts easily with oxovanadium(IV) mono- and dimeric complexes as solids and with the complexes dissolved in benzene, toluene, carbon disulphide, chloroform, dichloromethane and carbon tetrachloride, at room (or slightly higher) temperature. The reaction occurs for bi-, tri- and tetradentate Schiff base complexes, β-diketonate and similar (*e.g.* tropolonate) complexes of oxovanadium(IV). The monomeric oxovanadium(IV) complexes were prepared by standard methods ([4b] and references therein); the dimeric complexes by the method described in [5]. Satisfactory analytical data were obtained for all 16 dichlorovanadium(IV) complexes; additional analytical method was the reversed reaction:

$$VCl_2(chel)_2 + H_2O \longrightarrow VO(chel)_2 + 2HCl.$$

Here are presented ESR data for 6 selected typical complexes. ESR spectra were recorded on a JEOL JES-ME X-band spectrometer using a nuclear magnetometer MJ 110R and microwave frequency meter JES-SH-30X and ESR standards. The ESR parameters were corrected to the second order of perturbation theory. All reagents used were produced by MERCK.

Results and Discussion

$SeOCl_2$ is a good solvent for the dichlorovanadium(IV) complexes obtained by different methods, and these solutions are stable for several hours at room temperature in inert atmosphere.

$SeOCl_2$ has a rather high dielectric constant (ϵ = 46.0 against 9.2 for $SOCl_2$) and high dipole moment (2.64 Debye; 1.45 for $SOCl_2$) [6]. $SeOCl_2$ and $SOCl_2$ can act as Lewis bases, due to lone pairs on the oxygen, and as Lewis acids using 3d orbitals; a measure of the nucleophilic properties of the solvents is provided by the Donor Number (DN) [7]: DN for $SOCl_2$ = 0.4, DN for $SeOCl_2$ = 12.2. These strongly donating properties of $SeOCl_2$ as solvent occur in ESR spectra of the dichlorovanadium(IV) complexes dissolved in $SeOCl_2$. Because the dichlorocomplexes are six-coordinate it seems especially interesting to make comparisons of:

(1) $VO(chel)X$, $VO(chel')X_2$ or $VO(chel'')_2X$ six-coordinate addducts, where chel = tetradentate ligand, chel′ = tridentate ligand, chel″ = bidentate ligand, X = N-ethylimidazole, dissolved in N-ethylimidazole
(2) $VCl_2(chel)$, $VCl_2(chel')(SOCl_2)$ or $VCl_2(chel'')_2$ in $SOCl_2$
(3) $VCl_2(chel)$, $VCl_2(chel')(SeOCl_2)$ or $VCl_2(chel'')_2$ in $SeOCl_2$.

Selected ESR data are given in Table I.

The parameters P and κ were calculated using the expressions derived from second-order perturbation theory by McGarvey [8] and reformulated by Evans *et al.* [9]. The effective C_{2v}, C_s or other symmetry perturbation of the dominant C_{4v} (or D_{4h}) field in the complexes mixes the orbitals as follows:

$$\psi_G = a(3d_{z^2}) + b(3d_{x^2-y^2}) + c(4s).$$

For all investigated complexes a = 0, b = 1 except $VCl_2(chel'')_2$, where chel″ = five-membered O–O chelate ring, whereas $a \approx 1$, $b \approx 0$ for the complexes dissolved both in $SOCl_2$ and $SeOCl_2$. The c parameter is usually very small and may be neglected under most conditions [10].

On the basis of observed ESR parameters a comparison of the dichlorocomplexes is possible. There are three groups of complexes considering the effect of solvation:

(1) strong solvent effect: complexes of bi- and tridentate Schiff bases, β-diketonates
(2) weak solvent effect: complexes of tetradentate Schiff bases
(3) practically no solvent effect: complexes with five-membered chelate ring system, *e.g.* tropolone.

For group (1) the strongest solvent effect is connected with the *cis*-symmetry of the complexes in solution of $SeOCl_2$. Some of these complexes are *trans* in solids [1, 3] and give a mixture of *cis* and *trans* forms in $SOCl_2$ [4b]; in $SeOCl_2$, however, only

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TABLE I. ESR and Calculated Data for the Complexes, at Temperature 120 K. Parameters *A* and *P* are given in 10^{-4} cm^{-1} units.

Compound	Solvent	$-A_x$	$-A_y$	$-A_z$	g_x	g_y	g_z	P	κ^b
$VO(p\text{-}nas)_2(Eim)$	Eim	58	58	161	1.984	1.984	1.949	114	0.78
cis$VCl_2(p\text{-}nas)_2$	$SOCl_2$	47	47	145	1.954	1.954	1.960	111	0.68
cis$VCl_2(p\text{-}nas)_2$	$SeOCl_2$	64	64	179	1.980	1.980	1.923	124	0.78
$VO(aps)(Eim)_2$	Eim	59	57	162	1.983	1.981	1.947	115	0.77
cis$VCl_2(aps)(SOCl_2)$	$SOCl_2$	48	48	142	1.955	1.955	1.958	106	0.70
cis$VCl_2(aps)(SeOCl_2)$	$SeOCl_2$	65	65	173	1.975	1.975	1.933	118	0.82
$VO(eas)(Eim)_2$	Eim	52	50	160	1.971	1.969	1.954	122	0.68
cis$VCl_2(eas)(SOCl_2)$	$SOCl_2$	47	47	140	1.954	1.954	1.953	105	0.69
cis$VCl_2(eas)(SeOCl_2)$	$SeOCl_2$	66	66	175	1.974	1.974	1.935	119	0.82
$VO(acac)_2(Eim)$	Eim	62	62	167	1.982	1.982	1.946	116	0.80
cis$VCl_2(acac)_2$ [a]	$SOCl_2$	44	44	151	1.940	1.940	1.920	117	0.62
trans$VCl_2(acac)_2$ [a]	$SOCl_2$	48	48	154	1.968	1.968	1.862	108	0.70
cis$VCl_2(acac)_2$	$SeOCl_2$	64	64	180	1.980	1.980	1.930	126	0.78
$VO(salen)(Eim)$	Eim	54	54	158	1.977	1.977	1.955	116	0.74
trans$VCl_2(salen)$ [a]	$SOCl_2$	48	48	149	1.980	1.980	1.900	106	0.72
trans$VCl_2(salen)$	$SeOCl_2$	47	47	154	1.980	1.980	1.882	111	0.69
$VO(trop)_2(Eim)$	Eim	58	56	164	1.983	1.981	1.944	118	0.75
$VCl_2(trop)_2$ [a]	$SOCl_2$	110	102	~1	1.938	1.944	1.996	105	0.66
$VCl_2(trop)_2$	$SeOCl_2$	109	104	~1	1.938	1.944	1.998	106	0.66

[a] Ref. [4b]. [b] The spin-polarization parameter. *Abbreviations:* Eim = N-ethylimidazole; p-nas = condensation product of p-nitroaniline and salicylaldehyde (a bidentate Schiff base); aps = a condensation product of o-aminophenol and salicylaldehyde (a tridentate Schiff base); eas = a condensation product of ethanolamine and salicylaldehyde (a tridentate Schiff base); acac = acetylacetonate ligand; salen = condensation product of ethylenediamine and salicylaldehyde (a tetradentate ligand); trop = tropolonate ligand.

the *cis* form is present, as shown by ESR data. This is in good agreement with the suggestion given in [1] (the dependence of *cis–trans* equilibrium on dielectric constant of the solvent); the effect connected with the relatively strong donor–acceptor properties of $SeOCl_2$ is also detectable on the basis of calculated *P* parameters. The highest values of *P* observed for the *cis* complexes in $SeOCl_2$ are connected with strong steric and electronic interaction of the solvent with ligands and central ion and effective increasing charge on vanadium (theoretical *P* values for ^{51}V are: for V^0 85.7, for V^{+2} 128, for V^{+4} 172 × 10^{-4} cm^{-1} [8]). For group (2) complexes (*e.g.* with tetradentate ligands), the solvent effect is smaller. These complexes are *trans* in solution. In this case only the energy gap $d_{x^2-y^2} - d_{xy}$ becomes smaller for $SeOCl_2$ solvent.

A special problem is connected with group (3). These complexes being close trigonal prismatic in shape (D_3) have an $a_1(d_{z^2})$ ground state, $g_z \approx 2 > g_{x,y}$, $|A_\perp| > |A_\parallel|$. The d_{z^2} orbital does not interact with ligand atoms; practically no solvent effect is observed for these complexes which confirms the postulated geometry and electronic structure.

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