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Reactions of VCl_3, VCl_4 and TiX_4 (X = Cl, Br) with Benzofuroxan and its 5-Methyl-, 5-Chloro- and 5-Methoxi-derivatives. I.

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Abstract

By means of the reaction between VCl_3 and benzofuroxan the compound $VCl_3 \cdot 2C_6H_4N_2O_2$ was obtained, while in reaction with TiX_4 (X = Cl, Br) the compounds with stoichiometry $TiX_4 \cdot C_6H_4N_2O_2$ (X = Cl, Br) were obtained.

Furthermore, with some benzofuroxan derivatives (5-methyl, 5-chloro and 5-methoxi) the complexes $MCl_4 \cdot 2Y{-}C_6H_3N_2O_2$ (M = Ti, V; Y = CH_3O, Cl, CH_3), $TiCl_4 \cdot Y{-}C_6H_3N_2O_2$ (Y = CH_3O, CH_3) and $TiBr_4 \cdot Y{-}C_6H_3N_2O_2$ (Y = CH_3O, Cl, CH_3) have been isolated.

The compounds were characterized by elementary analysis, cryoscopic molecular weight determination in nitrobenzene, magnetic measurements and IR, Vis and EPR spectroscopy.

Introduction

In a previous work [1] we communicated the study of the reactions between $TiCl_4$, VCl_4 and $ZrCl_4$ with benzofuroxan (1:2), which led to the formation of addition compounds with stoichiometry $MCl_4 \cdot 2C_6H_4N_2O_2$. For the two former compounds with M = Ti, V, a *trans*-symmetry had been postulated, while for the zirconium compound a *cis*-symmetry was considered. More recent and detailed IR and EPR studies have obliged us to consider a *cis* molecular structure (C_{2v}) in every case.

Varying the reactions stoichiometry and using also the 5-methyl-, 5-chloro- and 5-methoxi-benzofuroxan derivatives, we have obtained a larger number of compounds which are listed in Table I.

The difficult systematization of these reactions reflects a very complicated chemical behaviour of the indicated ligands.

Results and Discussion

As previously described for the complexes of the tin tetrahalides with benzofuroxan derivatives [2], the bands assigned in the free ligands to the N–O stretching vibrations, present small shifts after the formation of the complexes, as a consequence of the weak donor ability of the benzofuroxan ligands.

TABLE I. Analytical Data[a] and Melting Point for the Compounds

Compound	Colour	%C	%N	Metal	X = Cl, Br	Melting point (°C)
$TiCl_4 \cdot 2CH_3O{-}C_6H_3N_2O_2$	orange	30.97(32.22)	10.54(10.73)	9.55(9.18)	28.05(27.17)	105 dec.
$TiCl_4 \cdot 2CH_3{-}C_6H_3N_2O_2$	yellow	33.98(34.32)	11.50(11.43)	9.78(9.77)	28.62(28.94)	105 dec.
$TiCl_4 \cdot 2Cl{-}C_6H_3N_2O_2$	yellow	27.13(27.16)	10.50(10.55)	9.12(8.93)	26.53(26.72)	103 dec.
$TiCl_4 \cdot C_6H_4N_2O_2$	yellow	22.14(22.12)	8.65(8.59)	14.03(14.70)	41.77(43.53)	132–135 dec.
$TiCl_4 \cdot CH_3O{-}C_6H_3N_2O_2$	dark red	22.90(23.63)	7.90(7.87)	13.45(13.46)	39.04(39.86)	115–116 dec.
$TiCl_4 \cdot CH_3{-}C_6H_3N_2O_2$	green	24.48(24.74)	7.91(8.24)	13.96(14.09)	40.56(41.73)	110 dec.
$TiBr_4 \cdot C_6H_4N_2O_2$	dark brown	14.60(14.31)	5.07(5.56)	9.60(9.51)	61.44(63.47)	178 dec.
$TiBr_4 \cdot CH_3O{-}C_6H_3N_2O_2$	dark brown	15.31(15.75)	4.84(5.25)	9.38(8.97)	56.51(59.90)	162 dec.
$TiBr_4 \cdot CH_3{-}C_6H_3N_2O_2$	dark brown	15.87(16.24)	5.33(5.41)	8.76(9.29)	59.90(61.75)	168 dec.
$TiBr_4 \cdot Cl{-}C_6H_3N_2O_2$	brown	13.95(13.39)	5.15(5.20)	9.72(8.90)	57.66(59.41)	172 dec.
$VCl_4 \cdot 2CH_3O{-}C_6H_3N_2O_2$	brown	30.47(32.04)	9.95(10.67)	10.43(9.70)	29.62(27.02)	85 dec.
$VCl_4 \cdot 2CH_3{-}C_6H_3N_2O_2$	brown	32.77(34.11)	10.99(11.36)	11.25(10.33)	29.81(28.77)	
$VCl_4 \cdot 2Cl{-}C_6H_3N_2O_2$	brown	27.40(27.01)	10.41(10.49)	10.38(9.55)	27.39(26.57)	
$VCl_3 \cdot 2C_6H_4N_2O_2$	dark brown	33.33(33.57)	12.94(13.04)	10.94(11.86)	23.41(24.77)	90–92 dec.

[a] % Found (calculated).

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By reacting $TiCl_4$ with $Y{-}C_6H_3N_2O_2$ (Y = H [1], CH_3O, CH_3) it was possible to synthesize the compounds with stoichiometries 1:1 and 1:2, while for Y = Cl the only product it was possible to isolate was the 1:2 adduct.

The compounds $TiCl_4{\cdot}2Y{-}C_6H_3N_2O_2$ are hexacoordinated monomers such as the experimental data indicate. A detailed discussion of the IR spectra enables us to propose a *cis*-symmetry for the compounds, it being impossible to obtain the Raman spectra owing to the strong sensitivity of the complexes against the laser radiation. The assigned bands of the Ti–Cl and Ti–O stretching vibrations are given in Table II.

For the compounds of $TiCl_4{\cdot}Y{-}C_6H_3N_2O_2$ (Y = H, CH_3O, CH_3) stoichiometry, the experimental data suggest a dimeric structure with chloro bridges between the titanium atoms, in such a way that the coordination around these titanium atoms will be octahedral. For $[TiX_4L]_2$ two symmetries, C_{2h}-*trans* and C_{2v}-*cis* for the ligands, would be possible. Although the bands corresponding to ν(Ti–X) are very strong and broad and very difficult to solve, the number of the stretching bands observed for the Ti–Cl and Ti–O bonds is very similar to those expected for C_{2h} symmetry (Table II). The relation observed between the terminal and bridged stretching vibrations lies in the expected range (0.66–0.72).

Observing the green colour of the 1:1 adduct formed between $TiCl_4$ and $CH_3{-}C_6H_3N_2O_2$, which is different to those observed in the rest of the synthesized compounds (yellow or red), we considered the possibility of a reduction of Ti(IV) to Ti(III) during the reaction. (A similar situation is described in the literature [3] for the complex formed by $TiCl_4$ with tricyclohexylphosphine, whose blue colour could suggest a reduction, but afterwards was experimentally checked as a diamagnetic compound.) To confirm this fact, we carried out magnetic susceptibility measurements. A value of 0.57 BM was obtained, which is much lower that the one expected for a d^1 system in a one octahedral ligand field. This value is interpreted as a temperature independent paramagnetism (TIP) [4–6].

By reacting $TiBr_4$ with the corresponding ligands, the compounds $TiBr_4{\cdot}Y{-}C_6H_3N_2O_2$ (Y = H, CH_3O, CH_3, Cl) are obtained. The cryoscopic molecular weight determination of the $TiBr_4{\cdot}C_6H_4N_2O_2$ compound, indicates a dimeric structure. We propose this same structure for the other three compounds although the experimental data were not very acceptable due to the considerable decomposition of the samples.

In Table II the stretching vibrations (IR) of the ν(Ti–Br) and ν(Ti–O) bonds are reported. The coordination number of six for the titanium atoms must also be attained here through the bridge bromine atoms (see also Table II).

By reacting VCl_4 with $Y{-}C_6H_3N_2O_2$ (Y = CH_3O, CH_3, Cl) the compounds with a 1:2 stoichiometry are obtained, and they present a big instability. The IR spectra show the presence of a very strong and broad band, clearly a multiple one, together with some other weak bands and shoulders which are assigned to the stretching vibrations of the vanadium–chlorine bonds.

It was not possible to assign more than one band to the stretching vibration of the vanadium–oxygen bond because it appears to be almost overlapped with the previously mentioned ν(V–Cl) vibration. The bands are reported in Table II.

Electronic Spectra of the Vanadium(IV) Compounds

Under the action of one octahedral ligand field, the fundamental term ^2D of vanadium(IV) is split into one lower term $^2T_{2g}$ and one higher ^2E_g, but the non-equivalent nature of the ligands, introduces at least one pseudotetragonal component to the ligand field, which splits the $^2T_{2g}$ term into two, $^2B_{2g}$ and ^2E_g, and also the term ^2E_g into $^2A_{1g}$ and $^2B_{1g}$. Then, two transitions in the visible region, $^2E_g \leftarrow {}^2B_{2g}$ and $^2B_{1g} \leftarrow {}^2B_{2g}$, would be expected.

The reflectance spectra of the complexes $VCl_4{\cdot}2Cl{-}C_6H_3N_2O_2$, $VCl_4{\cdot}2CH_3{-}C_6H_3N_2O_2$ and $VCl_4{\cdot}2CH_3O{-}C_6H_3N_2O_2$ present the bands reported below:

	$^2E_g \leftarrow {}^2B_{2g}$ (cm^{-1})	$^2B_{1g} \leftarrow {}^2B_{2g}$ (cm^{-1})
$VCl_4{\cdot}2CH_3O{-}C_6H_3N_2O_2$		20000
$VCl_4{\cdot}2CH_3{-}C_6H_3N_2O_2$	15380	21740
$VCl_4{\cdot}2Cl{-}C_6H_3N_2O_2$	14800	20000

The reaction between VCl_3 and $C_6H_4N_2O_2$ results in the formation of the compound $VCl_3{\cdot}2C_6H_4N_2O_2$. In the IR spectrum (Nujol) two bands appear at 375(s) and 314(m) cm^{-1} which are assigned to the terminal and bridge stretching vibrations of the vanadium–chlorine bond respectively, and one band at 426(w) cm^{-1} which is assigned to the ν(V–O) vibration (Table II). These values can be used to establish the stereochemistry of the compound, because for hexacoordinated complexes, the vanadium–chlorine stretching vibrations are expected in the range 380–300 cm^{-1}, while they appear in a higher range for penta- or tetracoordinated complexes [7].

When the IR spectrum is recorded in CH_2Cl_2 solution, the band previously assigned to ν(V–Cl) in the low frequency range disappears, and a new very strong and broad band appears at 453 cm^{-1}, which is typical for a trigonal bypyramid geometry (D_{3h}) and characteristic of pentacoordinated V(III) compounds [8, 9]. For this reason, we propose for the compound $VCl_3{\cdot}2C_6H_4N_2O_2$, a dimeric structure in which the

TABLE II. IR Spectra of Complexes[a]

	ν(M–O)	ν(M–X)$_{\text{terminal}}$	ν(M–X)$_{\text{bridge}}$	
$TiCl_4\cdot 2CH_3O-C_6H_3N_2O_2$	446m 414s	393vs 384sh 364vs		
$TiCl_4\cdot 2CH_3-C_6H_3N_2O_2$	443w 414s	396sh 382vvs 359sh		
$TiCl_4\cdot 2Cl-C_6H_3N_2O_2$	434m 421s	396vs 392vs 356m		
$TiCl_4\cdot C_6H_4N_2O_2$	432vs	405vs 390vvs	282m	
$TiCl_4\cdot CH_3O-C_6H_3N_2O_2$	433s	392vs 378vs 322w 316w	234m	
$TiCl_4\cdot CH_3-C_6H_3N_2O_2$	431vs	397vs 380vvs	254m	
$TiBr_4\cdot C_6H_4N_2O_2$		350vs 336vs 296vs,b	201m	
$TiBr_4\cdot CH_3O-C_6H_3N_2O_2$		352vs 335s 304vs 292vs	202sh	162m (δ BrTiBr)
$TiBr_4\cdot CH_3-C_6H_3N_2O_2$	446m	338vs 304vs 293vs	199sh	
$TiBr_4\cdot Cl-C_6H_3N_2O_2$	449w	350vs,s 338vs 328vs 290vs	203w	
$VCl_4\cdot 2CH_3O-C_6H_3N_2O_2$	418m	405sh 369vvs 329sh		
$VCl_4\cdot 2CH_3-C_6H_3N_2O_2$	417sh	395sh 374vvs 335sh		
$VCl_4\cdot 2Cl-C_6H_3N_2O_2$	414sh	396sh 374vvs 339m		
$VCl_3\cdot 2C_6H_4N_2O_2$ (solid) (CH_2Cl_2 solution)	426w	375s 453vs	314m	

[a] In cm^{-1}. X = Cl or Br. vvs = very very strong; vs = very strong; s = strong; m = medium; w = weak; sh = shoulder, b = broad.

vanadium atom is hexacoordinated in the solid state, while in a solution of CH_2Cl_2 it has a pentacoordinated configuration (*trans*-trigonal bypyramid).

EPR Spectra

The EPR spectra of the complexes $VCl_4\cdot 2Y-C_6H_3N_2O_2$ (Y = CH_3O, CH_3, Cl) in CH_2Cl_2 solution

TABLE III. EPR Parameters of the $VCl_4 \cdot 2Y{-}C_6H_3N_2O_2$ and $VCl_3 \cdot 2C_6H_4N_2O_2$ Complexes

	A_{iso} [a]	g_{iso}	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ [a]	$A_{\perp}$ [a]
$VCl_4 \cdot 2CH_3O{-}C_6H_3N_2O_2$	66.2	1.970	1.960	1.995	169.3	53
$VCl_4 \cdot 2CH_3{-}C_6H_3N_2O_2$	67.4	1.980	1.940	1.987	158.5	62.1
$VCl_4 \cdot 2Cl{-}C_6H_3N_2O_2$	68.8	1.966	1.946	1.991	154.9	60.5
$VCl_3 \cdot 2C_6H_4N_2O_2$	87.8	1.927	1.969	1.991	95.38	91.21

[a] Values are $\times 10^{-4}$ cm^{-1}.

at room temperature are isotropic and present eight lines due to the coupling of the unpaired electron with the ^{51}V ($I = 7/2$) nucleus.

Applying the Breit–Rabi equation [10] to our case, we obtain the values collected in Table III, which are comparable to those obtained for other V(IV) complexes [11].

The spectra of the complexes in CH_2Cl_2 solution at −160 °C are not well solved and it was not possible to distinguish the hyperfine lines; however, good spectra were obtained when the samples were diluted in KBr as polycrystalline powder and cooled to −160 °C. In this case, the spectra are anisotropic and two groups of eight lines, one for the H parallel and the other for the H perpendicular expected for one axial symmetry, are observed. The positions of the hyperfine lines can be calculated using the equations obtained by Stewart and Porte [12]. From the low temperature spectra, the values of the components of g and A tensors for the case of axial symmetry can be obtained (see Table III), and they are similar to those found for other V(IV) complexes with tetragonal distortion [11].

Substituting the values for the corresponding electronic transitions in eqn. (1):

$$g_{\parallel} = 2.0023 - \frac{8\lambda\nu}{\Delta E(b_{2g} - b_{1g})}$$
$$g_{\perp} = 2.0023 - \frac{2\lambda\nu}{\Delta E(b_{2g} - e_g)} \qquad (1)$$

the values $\lambda\nu$ can be calculated in the complexes: 106 cm^{-1} ($VCl_4 \cdot 2CH_3O{-}C_6H_3N_2O_2$), 144 cm^{-1} ($VCl_4 \cdot 2CH_3{-}C_6H_3N_2O_2$) and 112 cm^{-1} ($VCl_4 \cdot 2Cl{-}C_6H_3N_2O_2$), which compared with those of the isolated ion ($\lambda\nu = 250$ cm^{-1}) indicate a considerable participation of covalent bonds in the complexes. Furthermore, from these values can be inferred the existence of a higher bond delocalization in the complexes with the ligands $CH_3O{-}C_6H_3N_2O_2$ and $Cl{-}C_6H_3N_2O_2$.

The observation of the EPR spectrum at room temperature for a d^2 system is not common, due to the small spin–orbit relaxation time; however, it can be observed if the symmetry of the complex is low, as in the case of $VCl_3 \cdot 2C_6H_4N_2O_2$, from which relatively well solved spectra in CH_2Cl_2 solution are obtained, whose g and A parameters have the values given in Table III, comparable to those obtained for other V(III) complexes [11].

Experimental

All the reactions were carried out under anhydrous conditions, in an atmosphere of dry N_2, and using a glove-box for all the manipulations.

The benzofuroxan and the substituted benzofuroxans were prepared and purified by the methods described in the bibliography [13, 14].

$TiCl_4 \cdot 2Y{-}C_6H_3N_2O_2$ ($Y = CH_3O$, Cl, CH_3) and $TiCl_4 \cdot Y{-}C_6H_3N_2O_2$ (Y = H, CH_3O, CH_3)

These complexes were prepared by addition, at room temperature, of one solution of the ligand in CCl_4 or a mixture of $CCl_4{-}CH_2Cl_2$, over a solution of $TiCl_4$, recently distilled, in CCl_4. The precipitated solids were filtered off, washed with CCl_4 and hexane and dried in vacuum.

$TiBr_4 \cdot Y{-}C_6H_3N_2O_2$ (Y = H, CH_3O, Cl, CH_3)

$TiBr_4$ was synthesized by a procedure described in the literature [15]. Under similar conditions as those previously reported, some brown coloured solids were obtained, filtered off and after washing with CCl_4 or CCl_4–hexane, dried in vacuum.

$TiBr_4 \cdot C_6H_4N_2O_2$: Molecular weight (cryoscopy in nitrobenzene): 959.5 g mol^{-1}, (calculated for a dimeric compound: 1007 g mol^{-1}).

$VCl_4 \cdot 2Y{-}C_6H_3N_2O_2$ ($Y = CH_3O$, Cl, CH_3)

In an analogous way to those described previously, the reactions between VCl_4 [16] and the ligands were carried out. The obtained compounds are extraordinarily sensitive to moisture and must be manipulated very carefully. It was necessary to maintain the compound $VCl_4 \cdot 2Cl{-}C_6H_3N_2O_2$ at −20 °C in order to avoid its decomposition.

$VCl_3 \cdot 2C_6H_4N_2O_2$

The reaction was carried out in a dry and oxygen-free N_2 atmosphere, using the dry solvent (CH_2Cl_2) previously prepared by bubbling dry N_2 through it.

The mixture was kept under reflux for 48 h, and afterwards the excess VCl_3 was filtered off. The solvent was removed from the rest of the solution in vacuum, and a very dark brown solid was isolated; this solid contained a small amount of benzofuroxan which had not reacted and which was eliminated by stirring the product with dry CCl_4. After filtering, a brown solid was finally obtained whose analysis indicated that it was $VCl_3 \cdot 2C_6H_4N_2O_2$.

The IR spectra were recorded in a Nicolet 5DX spectrophotometer in the range 4000–200 cm^{-1}, using Nujol and hexachlorobutadiene, with CsI windows. The IR spectra in solution were recorded using a liquid cell with KBr windows. In the range of 500–150 cm^{-1} a Nicolet 60SX spectrophotometer with polyethylene pellets was used.

The diffuse reflectance spectra were recorded on a Beckman 24500 spectrophotometer, using magnesium oxide as a reference.

The EPR spectra were recorded on a Varian E-12 spectrophotometer at a microwave frequency of 9 GHz (X-band) equipped with a HP5342A frequency meter and a Bruker NMR Gaussmeter. The samples were introduced into quartz-glasses of 4 mm diameter. The low temperature spectra were obtained using a variable temperature cell.

The susceptibility magnetic measurements were made, using Faraday's method, with a Bruker Magnet B-M4 instrument.

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