Inorganica Chimica Acta, 33 (1979) 95–99
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Influence of the Oxo and Peroxo Ligands on the Stereolability of Chelated Hexa- and Heptacoordinated Species of Transition Metals

JEAN-YVES CALVÈS, JACQUES, E. GUERCHAIS, RENÉ KERGOAT and NADIA KHEDDAR*

Laboratoire de Chimie Inorganique Moléculaire, Faculté des Sciences et Techniques, 6, avenue Le Gorgeu, 29283 Brest-Cedex, France

Received August 3, 1978

The exchanges occurring in the $\{NbOCl_3(diket)\}^-$ *ions are not observed when the "oxo" ligand is replaced by a peroxide ion. This is the third example of rigidity in heptacoordinated complexes containing the "peroxo" group. This behavior is attributable to the nature of the bidentate peroxide ion, as observed previously in tungsten* [1] *and tantalum* [2] *peroxocompounds. Moreover another octahedral complex containing two "oxo" ligands,* $\{WO_2F_2(diket)\}^-$*, has been studies. The diastereotopic character of the two fluorines proves the rigidity of this ion in solution.*

Introduction

N.M.R. spectra exhibit exchange phenomena in various chelated molecules such as $SnCl_2(acac)_2$ [3, 4] {(acac): conjugated base of acetylacetone}, $MoO_2(diket)_2$ [5] and $TiX_2(diket)_2$ [6, 7] {(diket): conjugated base of a β-diketone, X: "fluoro" or 'chloro' ligand}. With terminal oxygen ligands, oxygen to metal π bonding proceeds from the overlap of the filled p_π orbitals of oxygen with the empty d_π orbitals of the metal; on the other hand the small size of the bidentate "peroxo" group leads to larger coordination numbers. So it seemed interesting to compare the influence of the "peroxo" and terminal "oxo" ligands on the dynamic properties of the compounds.

The substitution of the "oxo" ligand in the octahedral $\{(C_2H_5)_4N\}\{NbOCl_3(diket)\}$ [8] complexes, by the peroxide ion gives heptacoordinated species, for which many geometries and many isomers are possible. In this case, when the seven ligands are identical the differences in energy between idealized geometries (pentagonal bipyramid, capped octahedron...) are very small. Usually an averaged form is observed on the N.M.R. time scale. However, in this study the presence in the coordination sphere of the metal of different ligands in size and bonding should change the energy barriers between the different idealized geometries. Moreover, the presence of bidentate ligands prevents some twisting mechanisms.

The influence of the number of terminal "oxo" groups on the rigidity of the chelated species $\{WO_2F_2(diket)\}^-$ has been also examined.

Experimental

The different β-diketones used, R–CO–CH$_2$–CO–R′ were acetylacetone (acac H) with R = R′ = CH_3, dibenzoylmethane (dbm H) with R = R′ = C_6H_5, benzoyltrifluoroacetone (btfa H) with R = C_6H_5 and R′ = CF_3, thenoyltrifluoroacetone (ttfa H) with R = C_4H_3S and R′ = CF_3. The asymmetric β-diketone, trifluoro-1,1,1,methyl-5 heptanedione-2,4 was synthesised according to C. H. Hauser [10].

Preparation of Compounds

$\{(C_2H_5)_4N\}\{WO_2F_2(diket)\}$ *complexes*

Preparation and analytical data of these complexes were previously described [9].

$\{(C_2H_5)_4N\}\{NbOCl_3(diket)\}$ *complexes*

Their synthesis were reported in a previous paper [8]. In spite of the cautions taken for their preparation, a peak assignable to (diket H) was always observed on the N.M.R. spectra. The free ligand ratio ranged from 1.5 to 4.5%, and did not depend markedly on the solvent moisture – this was checked by adding small quantities of water to the solution – but on HCl produced by the reaction. When nitrogen was bubbled through the solution before the precipitation of the complexes a decrease in the (diket H) amount was observed; if acid was added the quantity of (diket H) increased. The complete disappearance of the organic molecule was very difficult because of the very important solubility of both the complexes and the free ligands in CH_3CN or CH_2-

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*Present address: Laboratoire de chimie minérale, Faculté des Sciences, 2, rue Didouche Mourad, Alger, Algérie.

ClCN which were the only suitable solvents for recrystallization.

{$(C_2H_5)_4N$}{$Nb(O–O)Cl_3(diket)$} complexes

The synthesis of tetraethylammonium aquotetrachlorooxoniobiate(V) {$(C_2H_5)_4N$}{$NbOCl_4(H_2O)$} was previously described [8].

5 g of this compound were dissolved in a hot aqueous solution of hydrogen chloride (about 80 ml) previously saturated with gaseous HCl, in order to prevent polymers formation. To the cooled solution (–40 °C) a few drops of hydrogen peroxide (30%) were added. The solution became red and it was saturated with gaseous HCl and kept at –30 °C during three hours. A small amount (800 mg) of yellow crystals of {$(C_2H_5)_4N$}{$Nb(O–O)Cl_4(H_2O)$} precipitated. They were characterized by their infrared spectrum which showed a band at 880 cm^{-1} assignable to the ν(O–O) vibration [11]. When the solid stayed in air atmosphere the intensity of the "peroxo" band decreased rapidly whereas an (Nb–O$_t$) (O$_t$: terminal oxygen) absorption appeared. Previous papers [1, 9] proved that N.M.R. spectra are more useful than elemental analysis to differentiate "oxo" from "peroxo" complexes as described for {WO_2F_2(diket)}$^-$ and {$WO(O–O)F_2$(diket)}$^-$ ions.

{$(C_2H_5)_4N$}{$Nb(O–O)Cl_4(H_2O)$} crystals were filtered off and dissolved again in 50 ml of freshly distilled acetonitrile. An equimolecular amount of β-diketone was added to the solution. The mixture was stirred for a few minutes at room temperature and the solvent was evaporated under reduced pressure. Red crystals with (dbm), orange coloured with (acac), (btfa) and (ttfa) precipitated. They were filtered off and dried over phosphorus pentoxide.

The niobium oxocomplexes synthesis and handling of compounds were carried out in a dry nitrogen atmosphere.

CH_3CN was distilled over CaH_2.

Spectroscopic Studies

Proton and fluorine N.M.R. spectra were run over the temperature range –30 °C to +80 °C with a JEOL C60 HL spectrometer, operating at 56.4 MHz for fluorine.

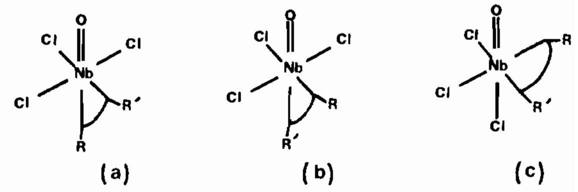
For proton, chemical shifts were measured relative to an internal reference of tetramethylsilane, and for fluorine relative to an external reference of trifluoroacetic acid.

Infrared spectra were recorded on a Perkin Elmer 225 spectrometer, using nujol mulls between cesium bromide windows.

Results and Discussion

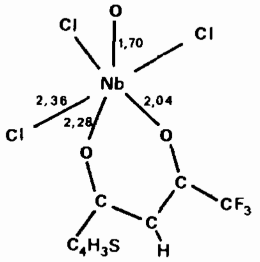
Niobium Oxo and Peroxochlorocomplexes

The existence of three isomers is possible for the {$NbOCl_3$(diket)}$^-$ ion in solution (scheme 1).



Scheme 1. Possible isomers of the {$NbOCl_3$-(diket)}$^-$ ion.

The crystal structure of {$(C_2H_5)_4N$}{$NbOCl_3$-(ttfa)} shows that in the solid state, the thienyl group is "*trans*" to the Nb=O bond (scheme 2) [12].



Scheme 2. Structure of the {$NbOCl_3(C_4H_3S$–CO–CH–CO–$CF_3)$}$^-$ ion (distances in Å).

At –40 °C, the proton spectrum of the acetylacetonate complex presents two methyl peaks of equal intensity. With increasing temperature, these lines broaden and coalesce at 17 ± 2 °C (Table I). This splitting occurring at low temperature indicates a slow dynamic exchange between the magnetically non equivalent methyl groups of the geometries a) or b). These previous geometries are not differentiable with symmetric β-diketones.

For the benzoyl- or thenoyltrifluoroacetonate solutions the fluorine N.M.R. spectra consist of three lines: two CF_3 peaks due to the complex itself and another one, very weak, due to the free ligands (Table I). This is consistent with the existence of at least two isomers in solution. The two signals attributable to the complex coalesce at room temperature, leaving the free ligand line unchanged.

The exact coalescence temperature is not convenient to determine because the relative intensities of the two peaks are very different. The same phenomenon is observed for the ring proton of the β-ketoenolate ion (Table I).

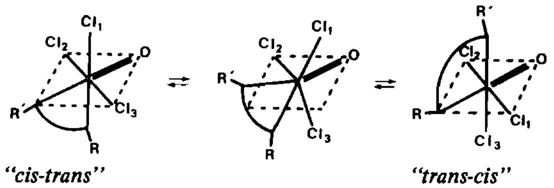
Coalescence temperature does not depend markedly on the dilution in the explored concentration range (1.8×10^{-2} to 0.3 *M* with the (acac) complex; 1.8×10^{-2} to 0.6 *M* with (btfa) and (ttfa) compounds). The addition of free ligand does not appear to have any influence on the rate of the exchange. These facts seem to prove that there is apparently no exchange between (diket H) and the oxochloroniobate ions, and are in favour of an intramolecular process.

TABLE I. N.M.R. Data for Niobium β-Diketonate Complexes in Acetonitrile Solution.

Compounds	T °C	$\delta(\overset{H}{\underset{/\ \backslash}{C}})^a$	$\delta(CH_3)^a$	$\delta(CF_3)^b$
$\{(C_2H_5)_4N\}\{NbOCl_3(dbm)\}$	−20 °C	7.12		
$\{(C_2H_5)_4N\}\{NbOCl_3(acac)\}$	−20 °C	5.85; 5.62^c	2.10 (S)^e; 1.98 (S) 2.01^c (vw)	
$\{(C_2H_5)_4N\}\{NbOCl_3(btfa)\}$	−37 °C	7.07 (86%)^d; 6.89 (12.5%) 6.80^c (1.5%)		−2.8 (86%); −1.7 (12.5%) −1.52^c (1.5%)
$\{(C_2H_5)_4N\}\{NbOCl_3(ttfa)\}$	−37 °C	6.9; 6.78^c; 6.60		−3.0 (87%); −2.1^c (2%); −1.95 (11%)
$\{(C_2H_5)_4N\}\{Nb(O–O)Cl_3(acac)\}$	−20 °C	5.97	2.25; 1.79	
$\{(C_2H_5)_4N\}\{Nb(O–O)Cl_3(ttfa)\}$	−30 °C	7.19; 6.88		−3.28; −2.28

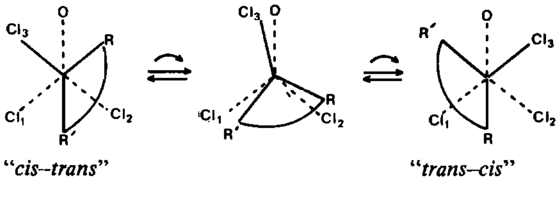
[a] Chemical shifts in ppm relative to internal TMS. [b] Chemical shifts in ppm relative to external CF_3CO_2H. [c] Signal of the free ligand. [d] Relative intensities based on total = 100. [e] The relative intensities have not been determined for the (acac) complex because the methyl peaks overlap with the protonated residue in CD_3CN. S: strong; vw: very weak.

Then the Ray–Dutt [2, 14, 15] and Bailar [14] mechanisms are envisageable. Because of its multiplicity the (Nb–O_t) bond is not expected to twist. The Ray–Dutt mechanism schematised below (scheme 3) conserves the "*cis–trans*" geometry in all the β-diketonato complexes. "*Cis*" and "*trans*" characterize the positions of the R and R′ groups relative to the terminal "oxo" ligand.



Scheme 3. Ray–Dutt mechanism.

A Bailar process (scheme 4) leads to the same results.



Scheme 4. Bailar mechanism.

Some other C_3 axis lead to "*cis–cis*" isomers of the type c) (scheme 1), allowed with (btfa) and (ttfa), but some rotations are not possible because of the chelated nature of the β-diketones.

With (acac) and (btra) the existence of both the "oxo" and "peroxo" compounds in solution provides a convenient study of the compared behavior of these complexes (Figures 1, 2). With (ttfa) the yield of peroxidation is smaller but the same phenomena are observed. As previously when the temperature increases the two CH_3 or CF_3 peaks of the oxo species coalesce, whereas the signals of the peroxo compounds are unchanged. These solutions slowly lose peroxide and the reaction is complete at about +60 °C preventing any study above this temperature.

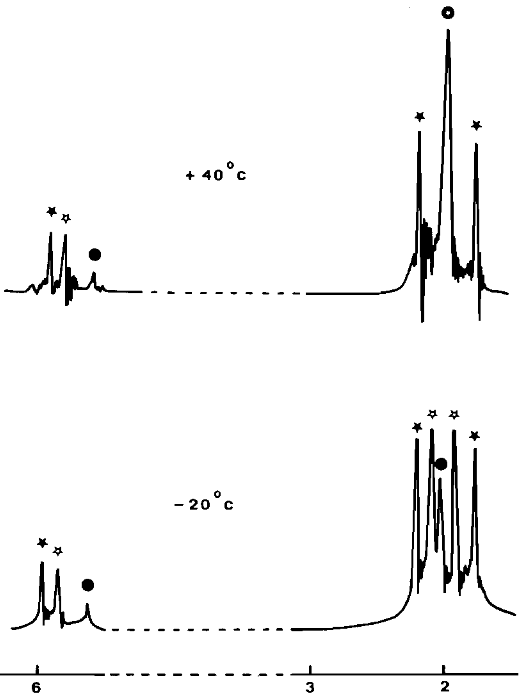


Figure 1. ^{1}H N.M.R. spectra of solutions containing the (acac) species; solvent: CD_3CN; internal reference TMS. ★ peroxided species, ☆ non peroxided species, ● free ligand.

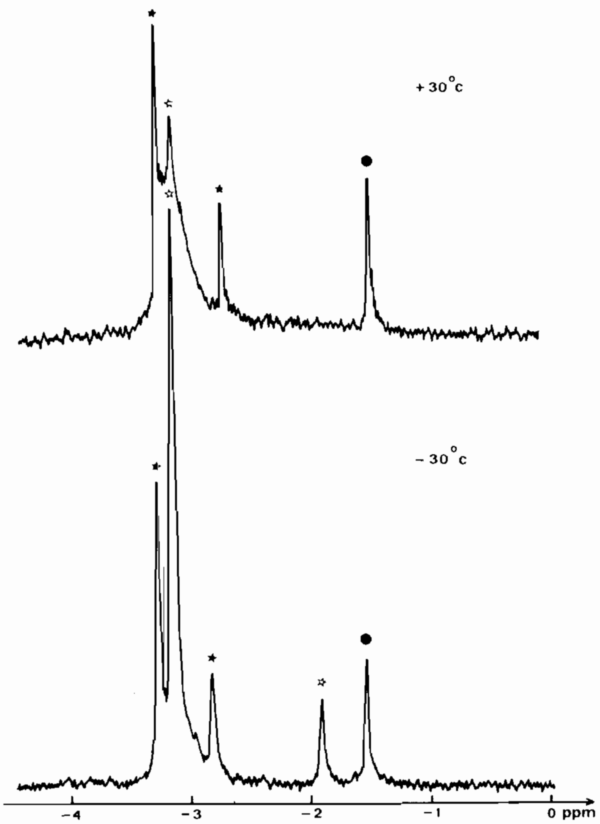


Figure 2. ^{19}F N.M.R. spectra of solutions containing the (btfa) species; solvent: CH_3CN; external reference CF_3CO_2H. ★ peroxided species, ☆ non peroxided species, ● free ligand.

With (acac), the presence, even at +50 °C, of two CH_3 peaks of equal intensity given by the same isomer proves the rigidity of the heptacoordinated $\{Nb(O{-}O)Cl_3(acac)\}^-$. This is due to the bidentate nature of the "peroxo" group which rules out some twisting mechanisms. With (btfa), R ≠ R′ (Figure 2), the presence of two CF_3 peaks of different intensities agrees with the existence of two isomers of the same geometry or with two different geometries. If this latter hypothesis is right, the characteristic stereolability of the hepta-coordination is strongly inhibited.

Tungsten Oxofluorocomplexes

In the temperature range −40 °C to +80 °C only one resonance assignable to the two "fluoro" ligands of $\{(C_2H_5)_4N\}\{WO_2F_2(diket)\}$ appears. However a permutation of the fluorine atoms by rapid conformatiomal interconversions may involve the observation of an averaged form. This hypothesis cannot be ruled out if the slow exchange conditions are not accessible by cooling.

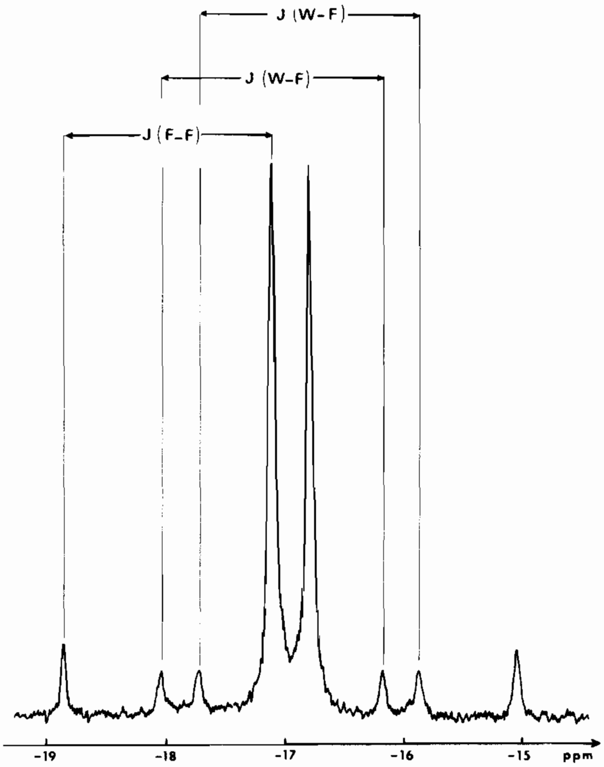
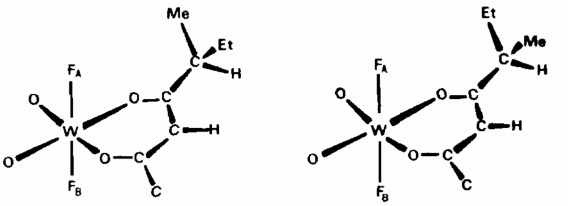


Figure 3. N.M.R. spectrum of fluorine on tungsten in $\{(C_2H_5)_4N\}\{WO_2F_2(CH_3CH^{*}_2CH(CH_3)COCHCOCF_3)\}$ (solvent: CH_3CN; t° = −20 °C; external reference CF_3CO_2H).

In particular a Ray–Dutt mechanism, keeping untwisted the multiple terminal oxygen to metal bonds may be suitable and is compatible with the retention of the tungsten–fluoride couplings. To solve this problem and corroborate the "*trans*-difluoro" structure we synthesized a β-diketonate complex bearing an asymmetric substituent: $CH_3CH^{*}_2CH(CH_3)COCH_2COCF_3$. The two "fluoro" ligands are then diastereotopic (scheme 5).



Scheme 5. Non-equivalence of the "fluoro" ligands.

They cannot be interchanged by any symmetry operation and they are magnetically different in homologous rotamers, even if the rotation around the asymmetric carbon–carbonyl carbon bond is rapid. The N.M.R. spectrum of these "fluoro" ligands is typical of an AB system (J_{AB} = 99 Hz) (Figure 3) while only one CF_3 resonance appears. Even when temperature raises (+70 °C) no exchange is observed and the "halogeno" ligands remain non equivalent. The inversion of the asymmetric carbon leading to the permutation of F_A and F_B fluorines involves the superposition of the two enantiomers in the racemic mixture. These results confirm the "*trans* difluoro" form and the rigidity of the $\{WO_2F_2(\text{diket})\}^-$ ion. This last property was previously observed in "peroxo" species such as $\{WO(O\text{–}O)F_2(\text{diket})\}^-$ [1].

Conclusion

The presence of the terminal oxygen to niobium multiple bond does not involve the rigidity of $\{NbOCl_3(\text{diket})\}^-$ octahedral species. Exchange phenomena take place in these ions and seem to proceed through an intramolecular mechanism. However, by complexing a bidentate "peroxo" group, the resulting heptacoordinated species lose their potential stereolability, and the motions occurring in the corresponding oxo species become impossible. It would be interesting to compare also the niobium and tantalum oxofluoro and oxochlorocompounds with their peroxided homologous. With the 'fluoro' ligand, only $\{(C_2H_5)_4N\}\{NbOF_3(\text{dbm})\}$ [16] and $\{(C_2H_5)_4N\}\{Nb(O\text{–}O)F_3(\text{dbm})\}$ [17] were isolated, but they are almost insoluble. Moreover the tantalum fluorinated oxo species are polymeric and they cannot be compared with the synthesised tantalum peroxo complexes which are also rigid [2].

The existence of a "*cis*-dioxo" group and a bidentate ligand bonded to tungsten in $\{WO_2F_2(\text{diket})\}^-$ ions leads to a "*trans*-difluoro" form because of the "*trans*" influence of the terminal oxygen to metal multiple bonds, and prevents the exchanges around the metal ion. This study shows that when two oxygen atoms are bonded together, the dynamic properties are altered in solution. The rigidity increases though the reverse is expected with heptacoordinated species. Moreover the $NbOCl_3L_2$ [18, 19] and $\{NbOCl_3(\text{diket})\}^-$ (this work) molecules, which contain only one oxygen atom, show rapid exchanges.

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