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OF ANTIMONY, NIOBIUM AND TANTALUM  
AND THEIR OXIDATION PROPERTIES

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SOME ORGANOPEROXO COMPLEXES OF ANTIMONY,  
NIOBIUM AND TANTALUM AND THEIR OXIDATION PROPERTIES

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**Abstract**

Several novel organoperoxo complexes of Nb(V), Ta(V) and Sb(V) have been synthesized and characterized. The complexes have the compositions  $[M(O_2)_2L Cl]$  and  $[M(O_2)_2L']$  [L = monodentate and bidentate, neutral ligand; L' = bidentate, uninegative ligand]. These complexes are very reactive to both organic and inorganic substrates. Niobium and tantalum complexes were found to oxidize phosphines and arsines to their oxides. These also oxidize olefins to epoxides under stoichiometric conditions while under catalytic conditions, ring opening of the epoxides occur producing  $\alpha$ -hydroxyketone when the substrate is trans-stilbene. The antimony complexes are decidedly inert towards oxidation.

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**Introduction** : There has been a great deal of interest in the peroxo complexes of transition metals because of their coordination chemistry as well as their role in synthetic organic and inorganic chemistry.<sup>1-12</sup> We have successfully employed peroxo complexes to generate glycine from allyl alcohol which is indeed an industrial aspect of the project.<sup>7</sup> The reactivity of the metal peroxides can be greatly modified by introducing metals of different sizes and ancillary ligands with different donor properties.<sup>5,6,12,13,14</sup> Peroxo complexes containing monodentate and bidentate auxiliary ligands were found to undergo oxygen transfer reactions,<sup>5,6,12</sup> however, those containing tridentate and quardridentate ligands were inert towards oxidation reaction.<sup>6,9,10,14,15</sup> Recently, we have reported the synthesis and properties of organoperoxo complexes of tin(IV).<sup>16</sup> There have been no studies whatsoever on peroxo complexes containing Sb(V), in particular. We have been interested in extending our studies to Sb(V), Nb(V) and Ta(V), with a view to afford comparison between dioxygen complexes of non-transition metals and those of transition metals. We report here the synthesis of these complexes along with their potential as oxidation catalysts. An attempt has been made to compare the reactivities depending on the nature and size of the metals used.

## **Experimental**

### *Reagents*

All chemicals were reagent grade and were used as supplied by Aldrich.

### *Physical Measurements and Elemental Analysis*

Infrared spectra (as KBr discs) were recorded on a Fourier-transform Perkin

Elmer 1750X instrument. Conductivities of  $10^{-3}$ M solutions in dimethylsulfoxide were measured at 25°C by using a 4020 digital conductivity meter and a dip-cell with platinized electrodes.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, in  $\text{CDCl}_3$ , were obtained with Zeol EX- 400 MHz NMR spectrometer. Tetramethylsilane was employed as an internal standard.

Carbon, hydrogen and nitrogen analyses were carried out by Microanalytiches Labor Pascher, Germany and also obtained from the Department of Soil Science, Universiti Putra Malaysia.

*General method for the preparation of  $[M(\text{O}_2)_2\text{LCl}]$  and  $[M(\text{O}_2)_2\text{L}']$  [ $M = \text{Sb(V)}$ ,  $\text{Nb(V)}$  and  $\text{Ta(V)}$ ];  $L = \text{OPPh}_3$ ,  $\text{OAsPh}_3$  and  $\text{ONC}_5\text{H}_5$ ;  $L' = \text{C}_9\text{H}_6\text{NO}$ ]*

$\text{SbCl}_3$  (0.005 mol) or  $\text{MCl}_5$  ( $M = \text{Nb(V)}$  and  $\text{Ta(V)}$ ) dissolved in ethanol (25  $\text{cm}^3$ ) was added to the solution of the ligand L or L' (0.005 mol) in the same solvent (30  $\text{cm}^3$ ). The mixture was heated with  $\text{H}_2\text{O}_2$  (30%, 50  $\text{cm}^3$ ). The product was filtered off, washed successively with ethanol and ether, and dried under vacuum over  $\text{P}_4\text{O}_{10}$ .

*Reaction of  $[M(\text{O}_2)_2\text{C}_9\text{H}_6\text{NO}]$  [ $M = \text{Nb(V)}$  and  $\text{Ta(V)}$ ] with triphenylphosphine (Reaction A)*

A solution of triphenylphosphine (0.01 mol) in THF (30  $\text{cm}^3$ ) was added to a suspension of (8) and (12) (0.005 mol) in the same solvent (75  $\text{cm}^3$ ). The mixture was kept under reflux in a nitrogen atmosphere and the progress of the reactions were monitored by TLC which indicated that the oxygen transfer reactions were complete in 8h for (12) while for (8), the solution was refluxed for 48h to complete the reaction. The solutions were filtered and the residue collected and was analyzed. The products

were isolated by evaporating the filtrates and were identified as  $\text{OPPh}_3$  [m.p. 154-156°C (lit. 157°C)].

*Reaction of 12 with trans-stilbene (Reaction B)*

Trans-stilbene (1.89, 0.01 mol) was added to a suspension of (12) (1.9 g, 0.005 mol) in  $\text{CH}_2\text{Cl}_2$  (200  $\text{cm}^3$ ). The mixture was kept under reflux and the progress of the reaction was monitored by TLC which indicated that the reaction was complete in 36h. The solution was filtered, the filtrate evaporated and the residue extracted with ether. Evaporation of the extract yielded 1.7 g of trans-stilbene oxide [m.p. 62-64°C (lit. 65-67°C)]

*Catalytic Reaction of (12) and  $\text{H}_2\text{O}_2$  with trans-stilbene (Reaction C)*

A 1.8 g quantity (0.01 mol) of trans-stilbene was added to 0.09 g of (12) suspended in 40  $\text{cm}^3$  of dioxane and 25  $\text{cm}^3$  of 30%  $\text{H}_2\text{O}_2$ . The mixture was heated under reflux at 90°C for 36h and filtered, and the filtrate evaporated to dryness. The residue was evaporated using a rotary evaporator a yellow solid (1.7 g, 80% yield) was identified as benzoin [m.p. 135-137°C (lit. 134-136°C)].

*Attempted Reactions of (4) with triphenylphosphine, triphenylarsine and trans-stilbene (Reaction D)*

Refluxing (4) with a stoichiometric amount of triphenylphosphine, triphenylarsine and trans-stilbene, respectively, in tetrahydrofuran for 48h failed to produce any reaction. Complex (4) was recovered.

## Results and Discussion

### *Syntheses and Spectroscopy*

Organoperoxo complexes of antimony were prepared by the oxidative addition of peroxy ligand to  $\text{Sb}^{3+}$  in all cases. These complexes are the first example of this kind in the literature. All of the complexes, (1) - (12), are diperoxo in nature as evident from the titration of methanolic solutions of the complexes with cerium (IV) which required 4 equivalent of ceric sulfate per mole of the complex indicating the presence of four active oxygen atoms in all of the complexes.<sup>17</sup> The molar conductance data indicated that all of the complexes were undissociated. The analytical and conductance data are presented in Table 1. These data are consistent with six-fold coordination of Sb(V), Nb(V) and Ta(V) complexes.

Infrared spectroscopic data are presented in Table 2. Complexes {(1), (5), (9)}, {(2), (6), (10)} and {(3), (7), (11)} show a decrease in  $\nu(\text{P}=\text{O})$ ,  $\nu(\text{As}=\text{O})$  and  $\nu(\text{NO})$ , respectively compared to free ligand values ( $\text{OPPh}_3$ ,  $1192\text{ cm}^{-1}$ ,  $\text{OAsPh}_3$ ,  $880\text{ cm}^{-1}$ ,  $\text{ONC}_5\text{H}_5$ ,  $1242\text{ cm}^{-1}$ ); this indicates coordination by the oxygen of the phosphine oxide, arsine oxide and pyridine oxide ligands. The far-infrared spectra display bands at  $420\text{-}470\text{ cm}^{-1}$  which tentatively attributed to the  $\nu(\text{M}-\text{O})$  modes.<sup>18</sup> In complexes (4), (8) and (12), the decrease in  $\nu(\text{C}=\text{N})$ , by  $53$ ,  $32$  and  $50\text{ cm}^{-1}$ , respectively, relative to the free ligand value ( $1610\text{ cm}^{-1}$ ) indicates coordination by the heterocyclic nitrogen.<sup>5,6,19</sup> These complexes display  $\nu(\text{M}-\text{N})$  modes at  $410\text{-}435\text{ cm}^{-1}$  in the far-infrared spectra of the complexes.<sup>18</sup> The  $\nu(\text{O}-\text{H})$  band at  $3405\text{ cm}^{-1}$  observed in free quinolin-8-ol disappears upon coordination indicating deprotonation, and coordination at the oxygen site. Complexes (1)-(3), (5)-(7) and (9)-(11) show bands at  $405\text{-}445\text{ cm}^{-1}$  which are tentatively attributed to the  $\nu(\text{M}-\text{Cl})$  modes.

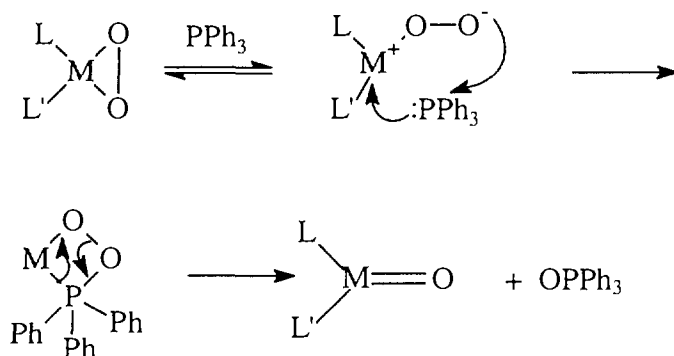
The metal peroxo grouping gives rise to three infrared and Raman active vibrational modes. These are predominantly O–O stretching ( $\nu_1$ ), the symmetric M–O stretch ( $\nu_2$ ) and the antisymmetric M–O stretch ( $\nu_3$ ). The characteristic  $\nu_1(\text{O–O})$  modes of (1)-(12) appear at 820-870  $\text{cm}^{-1}$  (Table 2). In particular the  $\nu_1$  mode decreases upon passing from niobium complexes (5)-(8) to the corresponding tantalum complexes (9)-(12) thus revealing the effect of size of the metals on O–O stretching modes. The complexes display  $\nu_3$  and  $\nu_2$  modes at 628-690 and 570-604  $\text{cm}^{-1}$ , respectively. The  $\nu_1(\text{O–O})$  stretching frequencies are decreased by replacing a given ligand by one which is a stronger donor. OAsPh<sub>3</sub> is more polar than OPPh<sub>3</sub> and is hence a stronger donor. This argument seems to apply in accounting for the lower  $\nu_1$  value observed for (2), (6) and (10) as compared to (1), (5) and (9), respectively.

*Reactivity:*

Peroxo complexes of antimony, niobium and tungsten were not explosive. These with the exception of antimony complexes liberate iodine on treatment with aqueous iodide. Compounds (8) and (12) were allowed to react with triphenylphosphine (Reaction A) which produced triphenylphosphine oxide. The infrared spectrum of the product showed band at 1190  $\text{cm}^{-1}$ , assigned to  $\nu(\text{P=O})$ .<sup>20</sup> The infrared spectrum of the metal residues of Reaction A showed disappearance of  $\nu_1(\text{O–O})$  band. The <sup>13</sup>C NMR spectrum of the product shows signals at 135.5, 132.3, 128.5 and 132.0 ppm which are assigned to the C-1, C-2, C-3 and C-4 carbons, respectively<sup>21</sup>. A possible reaction path is shown in Scheme 1. In order to obtain additional evidence for transfer of peroxo oxygen to PPh<sub>3</sub>, a blank experiment was performed in the absence of the complex under identical conditions, which failed to give the product. In addition compound (12) was more reactive compared to (8) as was evident from the reaction

time. This is consistent with the contention that tendency to expand coordination number increases with the increase of atomic number of metals in a group, and also in compliance with the fact that  $O_2^{2-}$  is less tightly held in (12) compared to that in (8) making the tantalum complexes more kinetically labile.

Scheme 1



Reaction B produced trans-stilbene oxide as evident from a strong infrared band at  $1055\text{ cm}^{-1}$  assigned to the C–O–C stretching mode and the methine absorption at 3.7 ppm in the  $^1H$  NMR spectrum as required for trans-stilbene oxide.

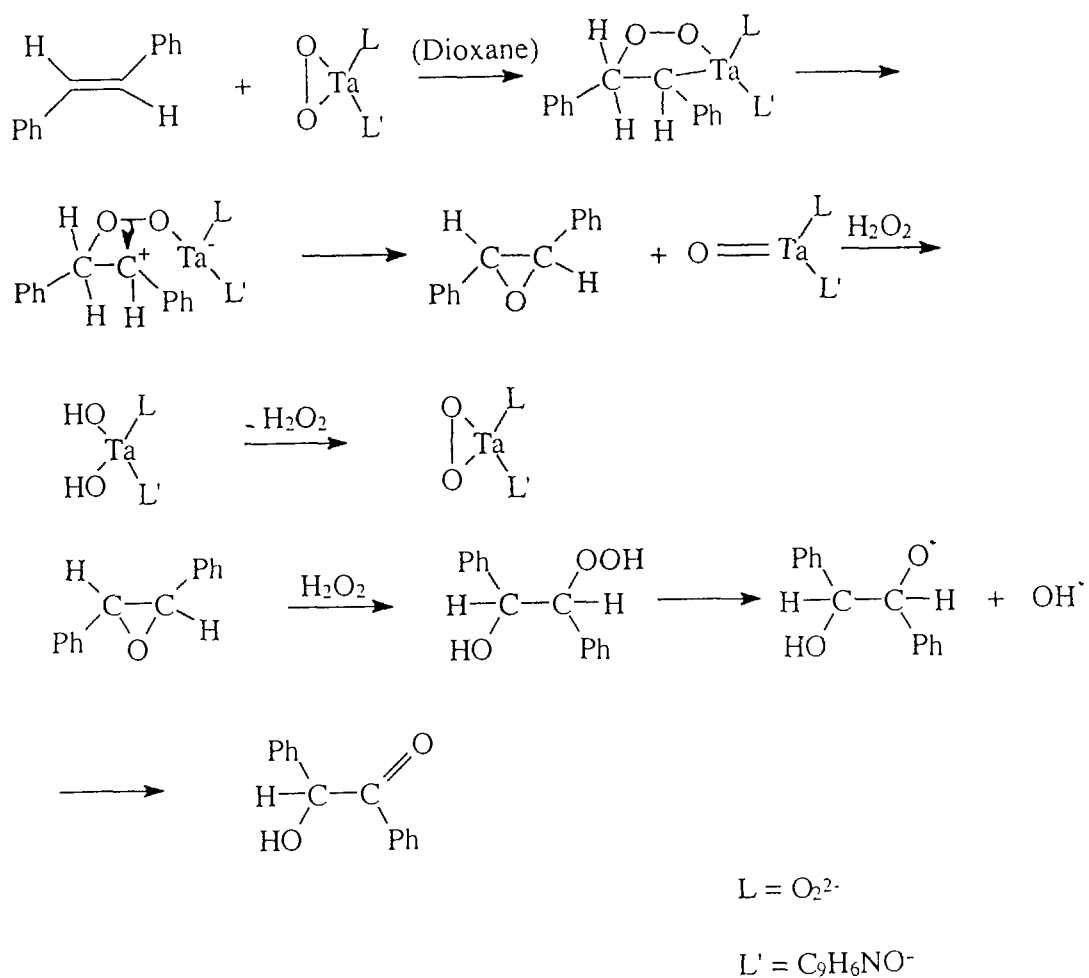
In reaction C, (12) was used to catalyze the oxidation of trans-stilbene by  $H_2O_2$  while the product was, however, benzoin. The presence of excess  $H_2O_2$  causes opening up of the epoxide ring and gives  $\alpha$ -hydroxy ketone in the end. The infrared spectrum of the product showed  $\nu(C=O)$  at  $1680\text{ (vs)}\text{ cm}^{-1}$  and  $\nu(O-H)$  at  $3385\text{ (s)}\text{ cm}^{-1}$ . The  $^1H$  NMR spectrum showed methine absorption at 5.5 ppm. A possible reaction path is shown in Scheme 2.

The organoperoxo complexes of antimony were stable thermodynamically as well as kinetically. The kinetic stability is attributed to the presence of extensive  $\pi$ - $d\pi$  bonding giving some double-bond character to the metal ligand bonding, thus making the complexes coordinatively saturated. This hinders nucleophilic substrates from becoming coordinated to antimony before formation of peroxy metalocycles to



facilitate the oxygen transfer. We have found a similar behavior with organoperoxo complexes of tin.<sup>1</sup> The inertness of organoperoxo complexes of non-transition metals toward oxidation reactions is attributed to their ineffectiveness to expand the coordination shell as would be necessary prior to oxygen transfer to both organic and inorganic substrates.

Scheme 2



## Acknowledgments

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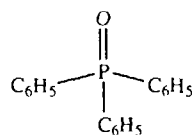
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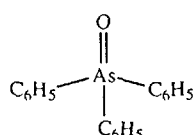
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( VCH Verlagsgesellschaft: Weinheim, 1987)

**Table 1. Analytical data and other physical properties of the complexes.**

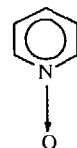
The organic moieties for the compounds are



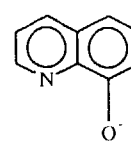
(1), (5), (9)



(2), (6), (10)



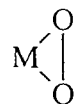
(3), (7), (11)



(4), (8), (12)

Compound Formula	No.	Colour of complex	Found %			Require %			Molar conductance Scm <sup>2</sup> mol <sup>-1</sup>
			C	H	N	C	H	N	
[Sb(O <sub>2</sub> ) <sub>2</sub> ·OPPh <sub>3</sub> ·Cl]	(1)	Colourless	42.8	2.9		43.3	3.0		3
[Sb(O <sub>2</sub> ) <sub>2</sub> ·OAsPh <sub>3</sub> ·Cl]	(2)	Colourless	38.9	2.8		39.7	2.8		1
[Sb(O <sub>2</sub> ) <sub>2</sub> ·ONC <sub>5</sub> H <sub>5</sub> ·Cl]	(3)	Colourless	18.7	1.5	4.3	19.0	1.6	4.4	2
[Sb(O <sub>2</sub> ) <sub>2</sub> ·C <sub>9</sub> H <sub>6</sub> NO]	(4)	Yellow	32.3	1.6	4.1	32.8	1.8	4.3	2
[Nb(O <sub>2</sub> ) <sub>2</sub> ·OPPh <sub>3</sub> ·Cl]	(5)	Yellow	45.3	2.9		45.9	3.2		4
[Nb(O <sub>2</sub> ) <sub>2</sub> ·OAsPh <sub>3</sub> ·Cl]	(6)	Yellow	43.2	3.0		43.7	3.0		3
[Nb(O <sub>2</sub> ) <sub>2</sub> ·ONC <sub>5</sub> H <sub>5</sub> ·Cl]	(7)	Colourless	20.5	1.6	4.4	20.9	1.7	4.9	1
[Nb(O <sub>2</sub> ) <sub>2</sub> ·C <sub>9</sub> H <sub>6</sub> NO]	(8)	Yellow	35.4	2.0	4.5	35.9	2.0	4.7	5
[Ta(O <sub>2</sub> ) <sub>2</sub> ·OPPh <sub>3</sub> ·Cl]	(9)	Colourless	38.3	2.4		38.7	2.7		2
[Ta(O <sub>2</sub> ) <sub>2</sub> ·OAsPh <sub>3</sub> ·Cl]	(10)	Colourless	35.6	2.3		35.9	2.5		3
[Ta(O <sub>2</sub> ) <sub>2</sub> ·ONC <sub>5</sub> H <sub>5</sub> ·Cl]	(11)	Colourless	15.7	1.2	3.3	16.0	1.3	3.7	1
[Ta(O <sub>2</sub> ) <sub>2</sub> ·C <sub>9</sub> H <sub>6</sub> NO]	(12)	Yellow	27.2	1.4	3.4	27.7	1.5	3.7	2

**Table 2. Infrared spectroscopic data for the complexes : band maxima (cm<sup>-1</sup>)**  
 Relative band intensities are denoted by : vs, very strong; s, strong ; m, medium; w, weak; sh, shoulder.  
 The symbol M<O<sub>2</sub> in the column heading represents



12

Compound Formula	No.	$\nu(\text{C}=\text{N})$	$\nu(\text{EO})$	$\nu_1(\text{O}-\text{O})$	$\nu_3(\text{M}<\text{O}_2)$	$\nu_2(\text{M}<\text{O}_2)$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{Cl})$	$\nu(\text{M}-\text{Cl})$
[Sb(O <sub>2</sub> ) <sub>2</sub> ·OPPh <sub>3</sub> ·Cl]	(1)		1080vs	850s	640s	570w	465m		440sh
[Sb(O <sub>2</sub> ) <sub>2</sub> ·OAsPh <sub>3</sub> ·Cl]	(2)		860m	830s	640vs	570w	470s		445m
[Sb(O <sub>2</sub> ) <sub>2</sub> ·ONC <sub>5</sub> H <sub>5</sub> ·Cl]	(3)	1560s	1202s	820m	672w	604s	455m		435s
[Sb(O <sub>2</sub> ) <sub>2</sub> ·C <sub>9</sub> H <sub>6</sub> NO]	(4)	1557s		828vs	628w	580w	450s	435m	
[Nb(O <sub>2</sub> ) <sub>2</sub> ·OPPh <sub>3</sub> ·Cl]	(5)		1070s	870vs	635sh	570m	435m		410w
[Nb(O <sub>2</sub> ) <sub>2</sub> ·OAsPh <sub>3</sub> ·Cl]	(6)		873m	860vs	690w	570s	425m		415m
[Nb(O <sub>2</sub> ) <sub>2</sub> ·ONC <sub>5</sub> H <sub>5</sub> ·Cl]	(7)	1545vs	1213vs	830s	675w	580s	430s		405w
[Nb(O <sub>2</sub> ) <sub>2</sub> ·C <sub>9</sub> H <sub>6</sub> NO]	(8)	1578vs		870vs	650w	598s	435s	410m	
[Ta(O <sub>2</sub> ) <sub>2</sub> ·OPPh <sub>3</sub> ·Cl]	(9)		1075vs	825s	640m	575w	425m		410w
[Ta(O <sub>2</sub> ) <sub>2</sub> ·OAsPh <sub>3</sub> ·Cl]	(10)		845s	815m	645s	570w	420m		405sh
[Ta(O <sub>2</sub> ) <sub>2</sub> ·ONC <sub>5</sub> H <sub>5</sub> ·Cl]	(11)	1540s	1205vs	820m	672w	578s	425s		405sh
[Ta(O <sub>2</sub> ) <sub>2</sub> ·C <sub>9</sub> H <sub>6</sub> NO]	(12)	1540s		825s	664m	565w	420w	410sh	