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Preparation, Characterization and Reactivity of Vanadyl(IV) and Uranyl(VI) Complexes with β,δ-Triketones and Ketophenols

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Some β,δ-triketones and β-diketophenols have been prepared and characterized. A series of mononuclear oxovanadium(IV) adducts with these ligands have been isolated and characterized. All these mononuclear complexes have a free coordination set and may act as ligands towards a second metal ion. The syntheses of dinuclear complexes using the mononuclear ones as ligands are reported. Their stereochemistry is discussed on the basis of ir, uv and magnetic data. Mono- and dinuclear complexes were tested as ethylene–propylene copolymerization catalysts.

Introduction

β,δ-Triketones and β-diketophenols have been used to synthesize homodinuclear complexes of Cu(II), Ni(II) and Co(II) [1–4] The choice of these easily available ligands [5, 6, 8] is due to their ability to function as dibasic acids. The oxovanadium(IV) dinuclear complexes have received less attention; in fact, they have been described only in one paper [7]. It is also well known that the uranyl(VI) ion forms a large variety of complexes with β-diketones [8]. In these complexes the linear O–U–O group is equatorially surrounded by five donor atoms, four from the two chelating β-diketones and one from the donor atom of the solvent used, giving rise to a pentagonal bipyramidal geometry. β,δ-Triketones and β-diketophenols represent a good opportunity to test if binuclear complexes containing the uranyl(VI) ion could be prepared.

This work relates with the syntheses of mononuclear and dinuclear complexes of oxovanadium(IV) and uranyl(VI), and to some polymerization tests performed with the aim to understand the effect of two interacting vanadium atoms in the catalytic complex.

Experimental

Five ligands were prepared: 1,5-bis(*p*-methoxyphenyl)-1,3,5-pentanetrione (H_2dmba), 1,5-diphenyl-1,3,5-pentanetrione (H_2dba), 2,4,6-heptanetrione (H_2daa), 2-acetoacetylphenol (H_2aap) and 2-benzoylacetylphenol (H_2dba). All of them were synthesized according to literature methods [5, 6].

Preparation of Mononuclear Complexes

The general procedure was as follows: the ligand (2 mmol) and LiOH (2 mmol) were dissolved in refluxing methanol (100 ml) under N_2 atmosphere. $VOCl_2$ (1 mmol) was added and the mixture was refluxed during 3 hr. The volume of the solution was reduced to 30 ml by evaporating part of the methanol. This caused the precipitation of solid materials which were separated by filtration, washed with methanol, and dried.

A synthesis of $VO(Hdba)_2$ was performed also by using the same concentration ratios, but absolute concentrations five times higher.

Table I summarizes analysis data, and magnetic and spectral properties of these complexes.

Preparation of Homodinuclear Complexes

Three methods have been used in different instances.

A) An air-free solution of mononuclear chelate (1 mmol) in pyridine (50 ml) was prepared. A methanol solution of $VOCl_2$ (1 mmol in 10 ml) and LiOH (2 mmol) was added. The solution was heated at 60 °C and maintained at this temperature for 3 hr.

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TABLE I. Elemental Analyses, Magnetic, Infrared and Ultraviolet Spectral Data of Mononuclear Oxovanadium Complexes.

Compounds	Colour	Analyses						μ (BM)	Infrared νC=O	νC=C	νV=O	Ultraviolet	
		C		H		V						d–d trans.	Other bands
		calcd.	found	calcd.	found	calcd.	found						
VO(Hdba)$_2$	yellow[a]	68.34	68.90	4.36	4.20	8.54	8.31	1.65	1620 1570	1510	990 900	770 580	440 390 290
VO(Hdba)$_2$	green[b]	68.34	68.40	4.36	4.40	8.54	8.80	1.68	1620 1570	1510	990	770 580	440 390 290
VO(Hdmba)$_2$	green	63.60	63.10	4.74	4.80	7.11	6.90	1.67	1665 1585	1520	985	775 585	430 410 330
VO(Hbap)$_2$OH	yellow	66.05	65.40	4.40	4.07			Diam.	1610 1585	1520	900		375 330 260
VO(Haap)$_2$	green	55.62	55.71	4.41	4.23			1.73	1615 1580	1510	995	760 590	350 320

[a] Prepared in dilute solution. [b] Prepared in concentrated solution.

TABLE II. Elemental Analyses, Magnetic, Infrared and Ultraviolet Spectral Data of Dinuclear Oxovanadium(IV) Complexes.

Compound	Colour	Preparation Method	Analyses						μ (B.M.)	I.R. (cm^{-1})			UV (nm)
			C%		H%		V%			νC=O	νC=C	νV=O	
			Calc.	Found	Calc.	Found	Calc.	Found					
(VO)$_2$(dba)$_2$	green	A, B	61.63	62.50	3.63	4.20	15.40	14.12	1.70	1590	1525	990	770, 580, 440, 390, 290
(VO)$_2$(dba)$_2$	red	C	61.63	62.00	3.63	3.45			1.65	1590	1525	990 900	775, 560, 440, 390, 290
(VO)$_2$(dmba)$_2$·2H$_2$O	green	A, B	56.01	56.27	4.42	4.57	12.46	11.58	1.61	1595	1520	985	775, 570, 430, 410, 330
(VO)$_2$(dmba)$_2$	red	C	58.31	58.02	4.09	4.02			1.58	1585	1520	985 890	775, 570, 430, 410, 330
(VO)$_2$(bap)$_2$·OH	yellow	A	56.07	56.97	3.37	4.13	15.70	13.16	1.98	1610 1590	1520	900	760, 590, 380, 340
(VO)$_2$(bap)$_2$·OH	yellow	B	56.07	56.20	3.73	4.00	15.70	13.56	1.98	1610 1590	1520	900	760, 590, 380, 340
(VO)$_2$(aap)$_2$·2H$_2$O	green	A, C	49.38	49.23	3.30	3.68			1.38	1615 1580	1520	995	760, 580, 350, 320
(VO)$_2$(daa)$_2$·H$_2$O	green	C	40.58	39.50	3.86	4.10			1.40	1535	1480	995	770, 580, 400, 390

TABLE III. Ethylene–Propylene Copolymerization Tests of Dinuclear Complexes.

Compound	Catalytic Activity	Propylene Content[a]	$[\eta]$[b]	$(r_1 \times r_2)$[c]
$(VO)_2(dba)_2$	8800	45	2.3	0.57
$(VO)_2(dmba)_2$	6400	44	2.3	0.66
$(VO)_2(bap)_2 \cdot OH$	7700	37	2.6	0.64
$(VO)_2(aap)_2 \cdot 2H_2O$	8500	40	2.4	0.55
$(VO)_2(daa)_2 \cdot H_2O$	5200	39	2.3	0.60
$V(acac)_3$	20800	51	2.3	0.48
$VOCl_3$	24400	50	2.4	0.46

[a] Determined by ir spectroscopy (% by weight). [b] Measured in decaline at 135 °C. [c] Determined by ir spectroscopy.

TABLE IV. Elemental Analysis, Infrared and Ultraviolet Spectral Data of Uranyl(VI) Complexes.

Compound[a]	Colour	Analyses				I.R. (cm^{-1})			UV (nm)
		C%		H%		νC=O	νC=C	ν_3 O–U–O	
		Calc.	Found	Calc.	Found				
$UO_2(Hdba)_2 \cdot H_2O$	orange	49.88	50.10	3.42	3.32	1620 1590	1510	910	475
$UO_2(Hdmba)_2 \cdot H_2O$	orange	48.61	48.46	3.84	3.78	1630 1590	1495	905	455
$UO_2(Hbap)_2 \cdot H_2O$	orange	47.00	47.28	3.13	3.42	1610 1590	1510	905	450, 370, 330
$UO_2(Haap)_2 \cdot H_2O$	orange	37.38	37.41	3.11	2.87	1610 1580	1520	900	460
$UO_2(Hdaa)_2 \cdot H_2O$	orange	29.47	29.88	3.51	3.62	1650 1585	1515	900	470, 400, 390

[a] The corresponding $UO_2(HL)_2 \cdot MeOH$ complexes are prepared by recrystallisation from MeOH.

The solvent was evaporated under reduced pressure. The residue was dissolved with methanol (20 ml) and the solution was stirred at room temperature under N_2 for 1 hour. After this time a precipitate was collected by filtration, washed with methanol, and dried.

B) The ligand (1 mmol) was dissolved in pyridine (50 ml). The solution was deaerated by bubbling N_2 and heated to 60 °C. To this warm solution $VOCl_2$ (1 mmol) and LiOH (2 mmol) were added. The mixture was stirred at 60 °C in N_2 atmosphere for 3 hr. The ame work-up as in method A followed.

C) The same amounts of reagents as in method B were used, but methanol was the solvent.

Table II gives the results obtained in the preparations of dinuclear complexes and the indication of the procedure used in preparing them, as well as their magnetic and spectral data.

Preparation of Dioxouranium Complexes

The ligand (2 mmol) and LiOH (2 mmol) were dissolved in 100 ml of a water/methanol mixture. A methanol solution containing 1 mmol $UO_2(NO_3)_2 \cdot 6H_2O$ was added. The solution was refluxed during 3 hr under stirring. The precipitate was filtered, washed with methanol or water, and dried.

For the ligand H_2aap only water was used as solvent.

For the ligand H_2bap only methanol was employed. One molecule of the solvent used to wash the precipitate remains coordinated to the metal atom. Results are collected in Table IV.

Ethylene–Propylene Copolymerization Tests

In each test the reactor was filled with 0.6 l of anhydrous n-heptane. Ethylene and propylene were bubbled into the solvent at rates of 1 and 2 l/min respectively. An air-free solution containing ethylene and propylene in a molar ratio 1:10 was so obtained after 1 hr. Diethylaluminum dichloride (3×10^{-3} *M*), n-butyl perchlorocrotonate (6×10^{-4} *M*) and the tested vanadium compound (6×10^{-5} *M*) were added. Dichloromethane was used to dissolve both mono- and di-nuclear complexes in 10–20 ml amounts. Immediately after the last addition an exothermic reaction started. The feeding of the monomers was continued for 60 min. After this no more heat was evolved. The addition of acetone (0.5 l) to the solution caused the precipitation of the ethylene–propylene co-polymer which was separated by filtration, dried at 100–110 °C, and weighed. The catalytic activities were then calculated as: (grams of polymer produced)/(grams of vanadium introduced). Table III shows the results obtained by testing some dinuclear complexes. The data for $V(acac)_3$ and $VOCl_3$ (which are presently used in industrial processes [9]) are also reported for a useful comparison. The same table shows the values for propylene content [10], intrinsic viscosity, and the product of the reactivity ratios [11].

Results and Discussion

Mononuclear Oxovanadium Chelates

When oxovanadium dichloride is reacted with β,δ-triketones or β-diketophenols in a 1:2 molar ratio in the presence of 2 mol of LiOH, mononuclear complexes are obtained, except for H_2daa. This ligand yields the dinuclear complex even when used in large excess with respect to $VOCl_2$. The formation of dinuclear complexes is the usual result when cations other than VO^{2+} (*e.g.*, Ni^{2+} and Co^{2+}) are used [3]. With ketophenols mononuclear chelates can be obtained, and are only stable at low temperatures.

The synthesis of VO(Hdba)$_2$ is very sensitive to reaction conditions. In fact, a yellow product is obtained from dilute solutions ($VOCl_2$: 10^{-2} *M*) and a green complex precipitates from mixtures having concentrations five-fold higher. It is also possible to obtain the yellow complex by heating a suspension of the green one during 2–3 hr. Elemental analyses and magnetic moments of the two samples are very close to each other (see Table I). A difference may be found in the ir spectra: the green complex shows a single V=O stretching band, while the yellow one has bands at 900 and 990 cm^{-1}. The differences in colour an ir spectra may probably be associated to V=O––– V=O interactions present in the yellow complex but not in the green one. UV spectra are identical.

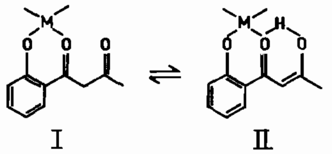
With H_2bap a yellow diamagnetic complex has been prepared. The formation of an oxovanadium(V) chelate in the absence of oxygen is difficult to explain because the oxidizing agent has not been identified. This complex shows only one V=O stretching band, at 900 cm^{-1}.

The ir spectra of all mononuclear complexes have essentially the same shape as the corresponding ligand with the addition of one or two bands (due to V=O stretching) at about 990 or 900 cm^{-1}. It is known that in acetylacetonate complexes C=O stretching vibrations lie at higher frequencies than C=C ones, as shown by ir spectra of ^{18}O and ^{13}C labeled molecules [12–16] and that C=C stretching bands are found at about 1500–1520 cm^{-1}. The strong band in the region 1665–1610 cm^{-1} may be associated with a hydrogen-bonded carbonyl group, while that in the region 1585–1570 cm^{-1} is due to a metal coordinated carbonyl group. We suggest that the band in the region 1520–1510 cm^{-1} corresponds to the νC=C vibration.

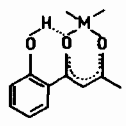
The electronic spectra in DMSO solutions show, in addition to bands in the uv region due to internal transitions in the ligand, d–d bands in the visible region at 580–590 nm and 760–775 nm. These bands are obviously absent in the spectrum of VO(Hbap)$_2$OH.

The values of the magnetic moments (1.65–1.73 B.M.) are those expected for magnetically diluted oxovanadium(IV) complexes.

β,δ-triketones have two identical coordination positions, while β-diketophenols may form two isomers:



A



B

The structure *B* seems to be the most probable because the electronic spectrum of VO(Haap)$_2$ is comparable to those of triketonates, and resembles more closely those of oxovanadium bis-β-diketonates than the one of oxovanadium bis(2-hydroxyacetophenonate). In addition, VO(Haap)$_2$ does not react with ethylenediamine to give the corresponding Schiff base complex, while structure *A* (if not completely in the enolic form) is expected to do. It must be noted that the ligand H_2aap is easily converted to the corresponding Schiff base.

Dinuclear Oxovanadium Chelates

Green or red oxovanadium dinuclear complexes may be obtained (depending on the reaction conditions) with the ligands H_2dba and H_2dmba, while only one type of complex is obtained with all other ligands (Table II). The infrared spectra of the red and green $(VO)_2$(dba)$_2$ and $(VO)_2$(dmba)$_2$ complexes are almost identical with regard to C=O and C=C bands, but strong differences are found in the νV=O region. The green compounds show only one band at 985–990 cm^{-1}, while the red ones have an additional strong band at 890–900 cm^{-1}, again suggesting V=O–––V=O interactions.

The electronic spectra of dinuclear complexes in DMSO solutions are similar and show two d–d bands at 760–775 nm and at 560–590 nm, indicating that the coordination geometries around the vanadyl ions are the same as in mononuclear chelates.

The magnetic moments of the dinuclear complexes are lower than the spin only values [17]; $(VO)_2(bap)_2OH$ instead behaves as if magnetically diluted (μ = 1.98 B.M.) according with the presence of a VO(V) and a VO(IV) in the molecule. The recorded magnetic values are higher than those of the corresponding Cu chelates. This is probably due to differences in exchange mechanisms in oxovanadium(IV) and copper(II) dimers [3, 4, 7] but the possibility of the presence of both VO(V) and VO(IV) in the same molecule cannot be discounted.

Several attempts to prepare heterodinuclear complexes starting from oxovanadium mononuclear chelates were unsuccessful, yielding the starting material or homodinuclear compounds. The nature of triketones and ketophenols, which offer two very similar O_2O_2 coordination sites, may be the reason for the difficulty to obtain heterodinuclear complexes. This behaviour differs from that of ligands which offer one O_2O_2 and one O_2N_2 site, easily forming stable heterodinuclear complexes.

Dioxouranium Chelates

When uranyl(VI) nitrate hexahydrate is treated with β,δ-triketones or β-diketophenols in 1:2 molar ratio in the presence of two moles of LiOH, the orange mononuclear complexes $UO_2(HL)_2 \cdot S$ (where H_2L is the ligand and S is water or methanol) are obtained. The infrared spectra of these complexes show in the 1660–1510 cm^{-1} region the three bands found also in oxovanadium complexes, indicating that the ligands are bound to the central atom in the same way. The strong band in the 915–900 cm^{-1} region is due to the asymmetric stretching of the O–U–O group. The uranyl(VI) ion is penta-coordinated in the equatorial plane. It was impossible to obtain homodinuclear complexes of the type $(UO_2)_2(L)_2S_2$, owing to the ion dimensions and to the equatorial geometry imposed by UO_2^{2+}. Attempts to prepare heterodinuclear complexes, using mononuclear chelates as ligands, failed. For example, from the reaction of $UO_2(Hdba)_2 \cdot H_2O$ with Cu acetate in hot methanol, the homodinuclear Cu complex was obtained. In any case a metal exchange occurs; the Cu(II) ion always substitutes the uranyl group in the complex.

Polymerization Tests

Table III shows the behaviour of dinuclear oxovanadium complexes as Ziegler–Natta catalysts. The unusual environment of the vanadium atom does not change significantly the features of the copolymer which is obtained, with respect to the widely used industrial catalysts. On the contrary, dinuclear compounds show much lower activities than $V(acac)_3$ and $VOCl_3$. The mononuclear oxovanadium complexes showed catalytic activities comparable to those of $V(acac)_3$ and $VOCl_3$.

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