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Bis(oxalato)dioxovanadate(V) and Bis(oxalato)oxoperoxovanadate(V) Complexes: Spectroscopic Characterization and Biological Activity

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Abstract Two structurally related vanadium(V) complexes, $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ and $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$, were thoroughly characterized by infrared, Raman, and electronic spectroscopies. The effect of both complexes on the viability of the human MG-63 osteosarcoma cells was tested using the MTT assay. The monoperoxo complex shows a very strong antiproliferative activity (at 100-μM concentration, this complex diminished the cell viability *ca.* 80 %), whereas the dioxo complex was inactive.

Keywords Vanadium(V) · Bis(oxalato) complexes · Peroxo ligand · Vibrational spectra · Electronic spectra · Osteosarcoma cells in culture

Introduction

The biodistribution, toxicology, and biological effects of vanadium, as well as its pharmacological activity, are areas of increasing research interest [1–3]. The potentiality of simple vanadium compounds and complexes as therapeutic agents has been repeatedly emphasized in recent years, and its insulin-mimetic [1–7], antitumoral [2, 3, 8–10], antiparasitic [11, 12], and antimicrobial activities [13] have been reported.

Although information about the metabolism of physiological amounts of vanadium in the higher forms of life, including man, remains scarce, some general aspects related to the absorption, transport, biological transformations, toxicity, excretion, and accumulation of vanadium are relatively well known [1, 14, 15]. In this context, the fact that bone seems to be the major sink for retained vanadium has been unambiguously demonstrated by numerous studies [14–16]. This fact determines the great interest to investigate the effects of vanadium compounds on osteoblast-like cells in culture.

As part of a general research project devoted to the search and characterization of new vanadium complexes with pharmacological activity, we have now investigated the spectroscopic behavior and the biological activity of two oxalato complexes of vanadium(V) on the proliferation of human MG-63 osteosarcoma cells in culture.

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Material and Methods

Materials

KVO_3 was purchased from Aldrich, $K_2C_2O_4\cdot H_2O$ and $H_2C_2O_4\cdot 2H_2O$ from Merck, and hydrogen peroxide from AnalQuim (Buenos Aires). Tissue culture materials were purchased from Corning (Princeton, NJ, USA), Dulbecco's modified Eagle's medium (DMEM) and TrypLE™ were from Gibco (Gaithersburg, MD, USA), and fetal bovine serum (FBS) was purchased from Internegocios SA (Buenos Aires). All other chemicals were from Sigma. MG-63 cell line was purchased from ATCC (CRL1427™).

Synthesis of the Complexes

$K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ was prepared by dissolving 1.38 g (10 mmol) of KVO_3, 1.84 g (10 mmol) of $K_2C_2O_4\cdot H_2O$, and 1.26 g (10 mmol) of $H_2C_2O_4\cdot 2H_2O$ in 20 mL of water at room

temperature. The mixture was stirred for 10 min, and then, the solution was left to evaporate in air. After a few days, yellow crystals were obtained. They were washed with small amounts of cold water and dried in air [17]. Their composition was confirmed by elemental chemical analysis (Calcd. for $C_4H_6O_{13}K_3V$: C, 11.15; H, 1.39 %; found: C, 11.12; H, 1.42 %).

The peroxo complex, $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$, was obtained by a procedure described by Schwendt et al. [18] as follows: the same quantities of KVO_3, $K_2C_2O_4\cdot H_2O$, and $H_2C_2O_4\cdot 2H_2O$ as above were dissolved in 30 mL of 5 % H_2O_2 at 0 °C. After stirring, and addition of 60 mL of cold acetone, a deep red oil was deposited at the bottom of the reaction vessel which was then stored in a refrigerator at 0 °C for 24 h, after which the oil appears transformed in a deep red crystal mass. The crystals were separated by filtration, washed with small portions of cold ethyl ether, rapidly dried in air, and then stored again in a refrigerator. The composition of the product was confirmed by elemental analysis (Calcd. for $C_4HO_{11.5}K_3V$: C, 11.96; H, 0.25 %; found: C, 11.90; H, 0.27 %).

To test the stability of the two complexes under the experimental conditions used in the biological assays, we analyzed the electronic absorption spectra of aqueous solutions of the complexes as a function of time. It could be established that the spectra were stable at least for 24 h.

Fresh stock solutions of the complexes were prepared in distilled water at a 100-mM concentration and diluted according to the experimental necessities.

Spectroscopic Characterization

Infrared spectra in the spectral range between 4,000 and 400 cm^{-1} were obtained with a Bruker EQUINOX 55 Fourier transform infrared spectroscopy (FTIR) instrument, using the KBr pellet technique. Raman spectra were measured on powdered samples using the FRA 106 Raman accessory of an IF66 Bruker spectrophotometer. A radiation of 1,064 nm from a Nd:YAG solid-state laser was used for excitation. Spectral resolution was ±4 cm^{-1} for both spectral measurements.

Electronic absorption spectra were measured on aqueous solutions of the complexes, with a Shimadzu model UV-300 spectrophotometer, using 10-mm quartz cells.

Cell Culture

MG-63 human osteosarcoma cells (CRL1427™) were grown in DMEM containing 10 % FBS, 100 U/mL penicillin, and 100 μg/mL streptomycin for 24 h at 37 °C in 5 % CO_2 atmosphere. Cells were seeded in a 75-cm^2 flask, and when 70–80 % of confluence was reached, the tumor cells were subcultured using 1 mL of TrypLE ™ per 25 cm^2 flask.

Evaluation of Cell Viability

The viability of cultured cells was analyzed using the 3-(4,5-dimethylthiazol-2-yl)-2,5-2,5-diphenyltetrazolium bromide (MTT) assay, according to Mosmann [19]. Briefly, cells were seeded in a 96-multiwell dish, allowed to attach for 24 h and treated with different concentrations of complexes at 37 °C for 24 h. After that, the medium was changed and the cells were incubated with 0.5 mg/mL MTT, under normal culture conditions for 3 h. Cell viability was marked by the conversion of the yellow tetrazolium salt MTT to a purple-colored formazan by mitochondrial dehydrogenases. Color development was measured spectrophotometrically in a Microplate Reader (7530, Cambridge Technology, Inc., USA) at 570 nm after cell lysis in DMSO (100 μL/well). Cell viability was plotted as the percentage of the control value.

Statistical Methods

At least three independent experiments were performed for each experimental condition. Results are expressed as %Basal and represent the mean±SEM. Statistical differences were analyzed using the ANOVA test.

Results and Discussion

Structural Characteristics of the Complexes

In $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$, and as shown schematically in Fig. 1, vanadium presents the same pentagonal bipyramidal coordination which is found in numerous other oxo-peroxovanadates(V) [20]. Besides, and as revealed by the structural analysis, this complex is not fully stoichiometric, containing small amounts of bis(oxalate)dioxovanadate(V) ions and H_2O_2 of crystallization. Therefore, its composition

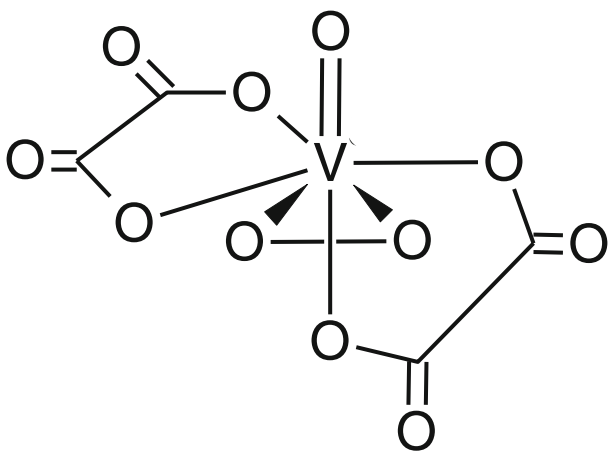

Fig. 1 Schematic drawing of the $[VO(O_2)(C_2O_4)_2]^{3-}$ complex anion

must be formulated as $K_3[VO_{1+x}(O_2)_{1-x}(C_2O_4)_2]\cdot(1/2-y)H_2O\cdot yH_2O_2$, $x \approx 0.2$ and $y \approx 0.1$ [17].

The complex anion $[VO_2(C_2O_4)_2]^{3-}$ in $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ presents a distorted octahedral geometry, in which the peroxo group shown in Fig. 1 is replaced by an oxo moiety, generating an angle of 104.35(10)° with the other oxo group. These two oxygen atoms have short V–O bonds (1.631(2) and 1.643(2) Å), indicating strong multiple bond character. The other four V–O bonds are longer (1.993(2) to 2.238(2) Å), with a substantial weakening of the two bonds *trans* to the oxo atoms [17, 21].

Spectroscopic Behavior

Vibrational Spectra

The FTIR and Raman spectra of $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ are presented in Fig. 2, and the proposed assignments are shown in Table 1. Their principal aspects are briefly commented as follows:

- The position of the ν(O–H) stretching vibration of the H_2O molecules suggests the presence of long hydrogen bridges [22, 23] in agreement with the structural data [21]. The corresponding deformational mode, $\delta(H_2O)$, is surely overlapped by the strong infrared (IR) triplet centered at *ca.* 1,680 cm^{-1}.
- The VO_2 group of the $[VO_2(C_2O_4)_2]^{3-}$ anion shows its stretching vibrations in the usual range [24], and also, the corresponding deformational mode, $\delta(VO_2)$, could be identified as a weak band in the Raman spectrum. Therefore, the overall spectroscopic behavior is in agreement with the experimentally found *cis* conformation for this group.
- The ν_{as}(C–O) vibrations of the oxalate groups are found at somewhat higher energies than in the previously investigated oxalate complexes of the types α-$M^{II}(C_2O_4)\cdot 2H_2O$ and β-$M^{II}(C_2O_4)\cdot 2H_2O$, in which this ligand acts as tetradentate [25, 26]. The important splitting of this vibrational mode is undoubtedly related with the presence of two structurally different oxalate groups in the structure.
- Other characteristic bands related to oxalate vibrations are also found in the usual spectral ranges [25–27].
- The comparison of the IR and Raman spectra of Fig. 2 and its analysis presented in Table 1 show some important intensity differences and, in certain cases, also shifts in band positions. This behavior can surely be related to factor group effects [28, 29]; as in the present case, the consideration of correlation field effects derived from the factor group C_{2h} indicates that IR and Raman bands belong to phonons of different symmetries (A_u and B_u for the IR modes, A_g and B_g for the Raman modes).

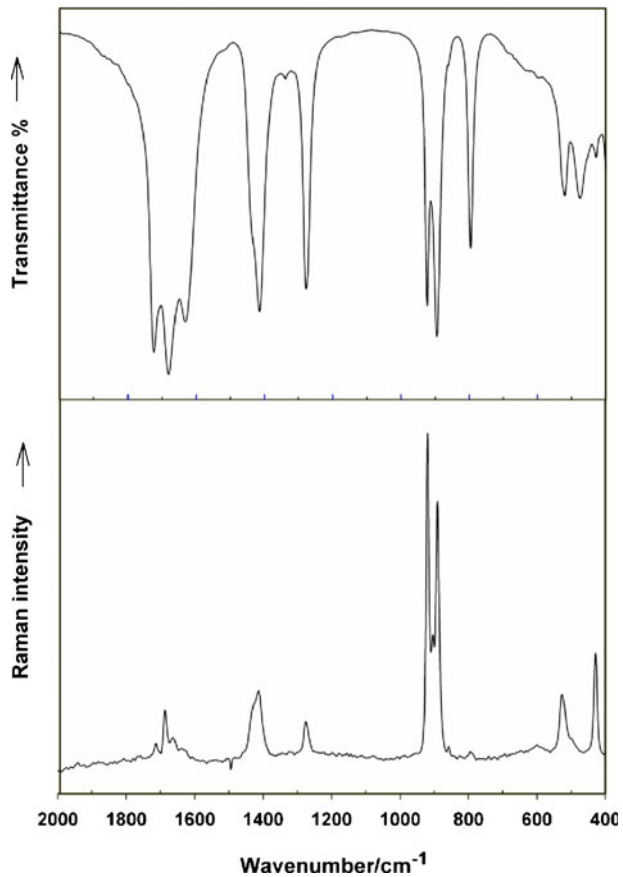

Fig. 2 FTIR (*above*) and FT-Raman (*below*) spectra of $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ in the spectral range between 2,000 and 400 cm^{-1}

Table 1 Assignment of the vibrational spectra of $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$

IR	Raman	Assignment
3,548 vs		ν(OH)
1,724 vs	1,715 w	ν_{as}(C–O)
1,681 vs	1,687 m	ν_{as}(C–O)
1,632 vs	1,666 w	ν_{as}(C–O)
1,414 vs	1,430 sh, 1,415 s	ν_s(C–O)+ν(C–C)
1,338 vw, 1278 vs	1,277 m	ν_s(C–O)+δ(OCO)
924 vs	923 vs	$\nu_s(VO_2)$
	902 w	ν(C–C)
895 vs	887 s	$\nu_{as}(VO_2)$
796 s	795 w	δ(OCO)+ν(CC)
519 m, 475 m, 428w	528 m, 429 m	δ(OCO)+ρ(OCO)
	364 w	$\delta(VO_2)$

Band positions in per centimeter

Intensity and form of the bands, *vs* very strong, *s* strong, *m* medium, *w* weak, *vw* very weak, *sh* shoulder

The vibrational spectra of the peroxo complex, $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$, is shown in Fig. 3, and the proposed assignment, presented in Table 2, is briefly discussed as follows:

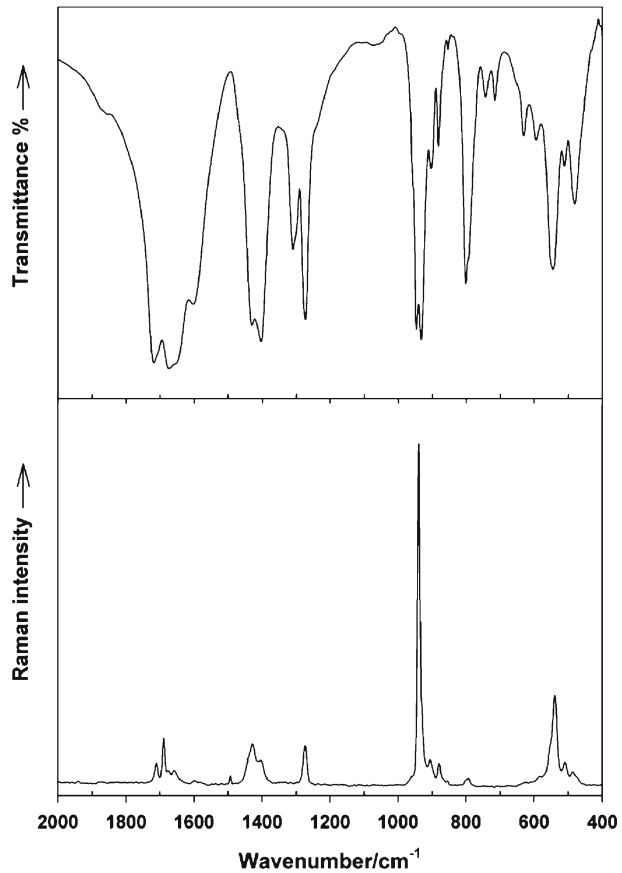

Fig. 3 FTIR (*above*) and FT-Raman (*below*) spectra of $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$ in the spectral range between 2,000 and 400 cm^{-1}

Table 2 Assignment of the vibrational spectra of $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$

IR	Raman	Assignment
3,475 s, 3,430 sh		ν(OH)
1,719 vs	1,711 w	ν_{as}(C–O)
1,673 vs, 1,658 sh	1,689 m, 1,658 vw	ν_{as}(C–O)
1,603 vs	1,600 vw	ν_{as}(C–O)
1,430 s, 1,403 vs	1,428 m, 1,405 sh	ν_s(C–O)+ν(C–C)
1,309 s, 1,273 vs	1,273 m	ν_s(C–O)+δ(OCO)
947 vs, 933 vs	939 vs	ν(V=O)+ν(O–O)
903 w	905 vw	ν(C–C)
882 m, 853 vw	880 w	ν(C–C)+δ(OCO)
801 vs		ν(C-C)+δ(OCO)
743 w, 715 w		δ_{ring}
631 w		ν(V–O_{per})
594 w		δ(OCO)
545 s	539 s	ν(V–O_{per})
511 w, 481 m	510 w, 486 vw	δ(OCO)+ρ(OCO)

Band positions in per centimeter

Intensity and form of the bands, *vs* very strong, *s* strong, *m* medium, *w* weak, *vw* very weak, *sh* shoulder

- In this case, the position of the ν(O–H) stretching vibrations suggests somewhat shorter hydrogen bonds [22, 23], and also here, the $\delta(H_2O)$ mode is overlapped with the strong oxalate vibrations.
- The oxalate vibrations are found at similar energies than in the dioxo complex, and the ν_{as}(C–O) mode is also clearly splitted. Interestingly, in this case also, the two IR bands involving the ν_s(C–O) vibrations show important splitting, suggesting that the presence of the peroxo group affects in a stronger way the oxalate vibrations.
- For the analysis of the vibrations of the peroxo groups and of the V–O_2 motions, it is usual to admit that the metal peroxo grouping behaves as an equilateral triangle with local C_{2v} symmetry [30]. For this grouping, three active IR and Raman bands are expected. From these vibrations, the $\nu_1(A_1)$ mode has, essentially, the characteristics of a O–O stretching, whereas $\nu_2(A_1)$ is fundamentally the symmetric V–O stretch, partially coupled with the O–O stretching. Finally, $\nu_3(B_1)$ basically originates in the antisymmetric V–O stretch. In agreement with this simple model, the strong band that is always seen in all peroxo complexes between 800 and 930 cm^{-1} must be assigned to the ν_1 (O–O stretching). Notwithstanding, in the present case, this spectral range is dominated by the ν(V=O) stretching vibration. Therefore, we admit that the strongest Raman line (939 cm^{-1}) and the corresponding IR doublet (947,933 cm^{-1}) involve both vibrational modes. From the other two expected peroxo vibrations, the ν_3 mode is only seen in the IR spectrum as a weak band (631 cm^{-1}), whereas the ν_2 vibration is found in both spectra as a relatively strong signal.

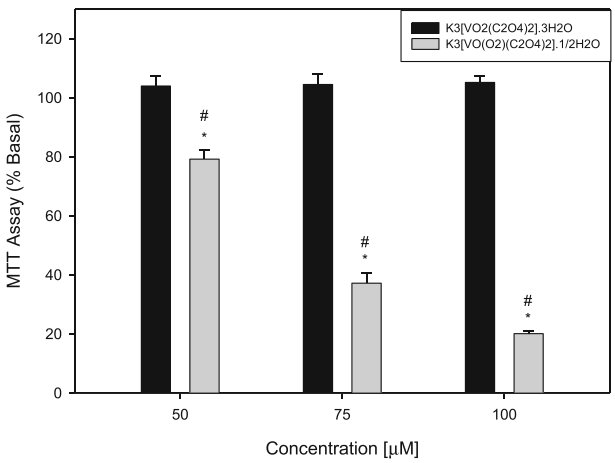

Fig. 4 Evaluation of the mitochondrial succinate dehydrogenase activity by the MTT assay in MG-63 cells in culture. Osteosarcoma cells were incubated with different doses of $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ and $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$ for 24 h at 37 °C. After incubation, cell viability was determined by the MTT assay. Results are expressed as percent (%) basal and represent the mean±SEM, $n=18$; *asterisks* (*) indicate significant differences versus control ($p<0.01$); *number signs* (#) indicate significant differences between samples ($p<0.05$)

Electronic Spectrum

The electronic spectrum of $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ presents a strong absorption band centered at 193 nm ($\varepsilon \sim$ 15,000 L mol^{-1} cm^{-1}) with a shoulder at about 285 nm ($\varepsilon \sim$ 2,000 L mol^{-1} cm^{-1}). On the other hand, the $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$ complex presents also the 193-nm band ($\varepsilon \sim$14,200 L mol^{-1} cm^{-1}) and a weaker one located at 440 nm ($\varepsilon \sim$300 L mol^{-1} cm^{-1}) that shows a slow decay to the visible region and is, therefore, responsible for the color of the complex.

The higher energy band is surely related to a charge transfer from the oxo (or dioxo) group to the central vanadium(V) atom. For comparison, it should be emphasized that in the case of the orthovanadate anion, VO_4^{3-}, this type of O → V charge transfer bands are found at 200 and 270 nm [31]. The second band has usually been assigned to a charge transfer from the π^* orbitals of the peroxo group to *d* orbitals of the central vanadium(V) unit and is evidently favored by the high charge of this center [20].

Effect of the Complexes on Cell Viability

Multiple biological and molecular actions of vanadium have been implicated in its inhibitory effects on various tumor cells [32], and considering the main accumulation of vanadium in bone-related cells in vertebrates, it was of great interest to determine the effect of the prepared vanadium complexes in osteoblast-like cells in culture.

In order to test the impact of the presence of a peroxo group in the oxovanadium(V) complex $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$, we compare its effect with those of $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ on the viability of the human MG-63 osteosarcoma cells. The tumor cells were exposed to different concentrations of both complexes, and the results can be observed in Fig. 4. This figure displays the effect of both complexes on the mitochondria metabolism of MG-63 osteosarcoma cell line. As can be seen, $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$ caused a concentration-related inhibition from 50 to 100 μM with statistically significant differences versus basal condition ($p < 0.01$). On the contrary, $K_3[VO_2(C_2O_4)_2]\cdot 3H_2O$ did not cause any inhibitory effect in the range of tested concentrations ($p < 0.01$).

It is evident that $K_3[VO(O_2)(C_2O_4)_2]\cdot 1/2H_2O$ is a very strong antiproliferative agent since at 100-μM concentration, the complex diminished the cell viability *ca.* 80 % ($p < 0.01$). These results clearly support the importance of the peroxo ligand in the coordination sphere of the metal for the antitumor activity.

In this context, it is also interesting to mention that some time ago, a series of vanadium(V) complexes of the type $[VO(O_2)L]^{n-}$ also showed interesting antitumor activity against L1210 murine leukemia. Besides, in these animal experiments, related V(V) complexes, lacking the peroxo ligand, are practically inactive [9, 33].

The presented results show again the potentiality of vanadium complexes as valuable anticancer agents, suggesting that more efforts should be invested on the synthesis and characterization of new complexes of this element and on the exploration of its pharmacological properties.

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