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PEROXOVANADATE (v) COMPLEXES

by

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Abstract: *Six new triperoxovanadate (v) complexes of the type* $M^{I}\{V(O-O)_3(AA)\}.nH_2O$ *and* $M^{II}\{V(O-O)_3(AA)\}_2.nH_2O$, M^{I} = *Liand* M^{II} = *Ca or Ba; (AA)=* 2,2 *-bypiridyl or* 1,10*-phenanthroline have been prepared. Molar conductances in aqueous solutions confirmed the* 1:1 *and* 1:2 *type of electrolytes. Assignments of the observed ir and uv frequencies are given compared with the corresponding peroxovanadate (v) complexes.*

INTRODUCTION

The present work deals with the synthesis and spectroscopic study of some new peroxovanadate (v) complexes. The compounds described here are of the type $M^{I}\{V(O-O)_3(AA)\}.nH_2O$ and $M^{II}\{V(O-O)_3(AA)\}_2.nH_2O$ where M^{I} = Li; and M^{II} = Ca or Ba; (AA) = bipyridine or phenanthroline. Similar compounds have been already prepared by the reaction of these ligands with solution of metavanadates in hydrogen peroxide[1].

There are a number of papers[1-3] dealing with peroxo complexes of the type $K\{M^{v}(O-O)_3(AA)\}.nH_2O$ $\{M^{v}$ = Nb or Ta and V; (AA) = bipyridine or phenanthroline$\}$. These compounds are derived from the tetraperoxovanadates (v) by substitution of one peroxo group by one bidentate ligand. *Fergusson et al*[4] showed the isomorphism of compounds such as $K_3\{M^{v}(O-O)_4\}$ (M^{v}= V, Cr, Nb, or Ta). Analogous compounds have been studied by *Stomberg*[5] who demonstrated that the chromium compound has a quasidodecahedral structure. In addition x-ray data show that the structure of $K\{Nb(O-O)_3$ phen.$\}.3H_2O$ is that of a distorted dodecahedron[6].

EXPERIMENTAL SECTION

Molar conductances were measured using a conductivity bridge (Model RC 216B2). The ir spectra were obtained on Beckman-IR5A (4000-600 cm^{-1}) and Perkin - Elmer 180 (1000-200 cm^{-1}) spectrophotometers with potassium bromide discs containing 1% of the compounds, Nujol mulls and polyethylene plates.

The uv-vis spectra were recorded on a Zeiss PMQ II spectrophotometer using freshly prepared aqueous solutions of the compounds (concentration *ca.* 10^{-5} M).

Preparations. The triperoxovanadate (v) complexes were prepared according to the general method used by *C. Djordjevic and N. Vuletic*[2] for triperoxoniobates and - tantalates. This method was also applied by *J. Sala - Pala* and *J. E. Guerchais* for the preparation of triperoxovanadates[1].

The compounds obtained in this way are hydrated with two or three water molecules. Attempts to obtain anhydrous compounds failed as the yellow or orange crystals of the peroxo complexes were transformed into a dull yellow powder when kept over phosphorous pentoxide for at least two days. Attempts to recrystallize the complexes from hydrogen peroxide solutions, without decomposition, also failed. The compounds are fairly stable under refrigeration.

Analyses. The peroxide determination was carried out by the addition of sulphuric acid to an aqueous solution of the compound containing an excess of potassium iodide. The iodine formed was titrated with standard thiosulphate solution.

The determination of carbon, nitrogen and hydrogen was done using a Perkin - Elmer 240 Elemental Analyser. The other elements were determined according to ordinary analytical methods[7].

The analytical data for the compounds are collected in Table 1.

RESULTS AND DISCUSSION

The compounds are soluble in water and hydrogen peroxide and insoluble in the common organic solvents. They decompose on heating evolving oxygen.

These compounds, when compared to the corresponding peroxo derivatives of other transition metals, are remarkably stable and can be kept for weeks in a dark dry atmosphere.

The values of the molar conductances of aqueous solutions of the

TABLE I

Analytical Data

Compound	Calculated (%)								Found (%)							
	C	H	N	Li	Ca	Ba	V	O_{per}	C	H	N	Li	Ca	Ba	V	O_{per}
$Li\{V(O - O)_3bipy\}.3H_2O$	32.98	3.84	7.69	1.90	—	—	13.99	13.18	33.68	3.82	7.80	1.85	—	—	13.90	13.15
$Ca\{V(O - O)_3bipy\}_2.2H_2O$	35.20	2.93	8.20	—	5.87	—	14.93	14.06	34.75	3.12	7.98	—	5.52	—	14.89	13.98
$Ba\{V(O - O)_3bipy\}_2.2H_2O$	30.78	2.56	7.18	—	—	17.61	13.07	12.31	30.26	3.25	6.96	—	—	17.58	13.01	12.30
$Li\{V(O - O)_3phen\}.2H_2O$	38.90	3.24	7.56	1.87	—	—	13.76	12.96	39.08	3.49	7.58	1.82	—	—	13.75	12.90
$Ca\{V(O - O)_3phen\}_2.2H_2O$	38.51	2.67	7.48	—	5.35	—	13.61	12.82	39.07	3.01	7.50	—	5.39	—	13.59	12.80
$Ba\{V(O - O)_3phen\}_2.2H_2O$	34.08	2.36	6.62	—	—	16.24	12.04	11.35	34.15	2.41	6.60	—	—	16.29	11.97	11.30

compounds (concentration 4×10^{-3} M) at 20°C are shown in Table II. These values are in agreement with those of the literature and confirm that the compounds are 1:1 and 1:2 electrolytes.

TABLE II

Molar conductivities (Λ) (in ohm^{-1} cm^2 mol^{-1})

Compound	Λ
$Li\{V(O — O)_3(bipy)\}.3H_2O$	133
$Ca\{V(O — O)_3(bipy)\}_2.2H_2O$	252
$Ba\{V(O — O)_3(bipy)\}_2.2H_2O$	265
$Li\{V(O — O)_3(phen)\}.2H_3O$	105
$Ca\{V(O — O)_3(phen)\}_2.2H_2O$	221
$Ba\{V(O — O)_3(phen)\}_2.2H_2O$	233

The general pattern of the ir spectra of the compounds (Table III) is similar to that of the spectra of the corresponding triperoxovanadate complexes.

As has been pointed out[8,9], the triperoxo group absorbs in two different regions. The strong bands in the 800-930 cm^{-1} region are assigned to O–O stretching vibrations, while the absorptions in the 600-650cm^{-1} region are assigned to $\overline{\text{O-V-O}}$ vibrations[10]. These bands have also been observed in the spectra of tetraperoxovanadates[4], triperoxovanadates[1], triperoxoniobates and -tantalates[2].

It has been demonstrated[11-13] that the spectra of bipyridyl complexes agree closely with those of 2-substituted pyridines in general. The spectra of iron (II) complexes with bipyridyl, phenanthroline, and related α-diimine ligands have been discussed by *Bush* and *Bailar*[14].

On coordination to the metal ion the ring frequencies (1600-1000 cm^{-1}) undergo shifts to higher wave numbers compared to those in the spectrum of the free ligand. Slight perturbations of the C — H in-plane deformation modes (β–CH) are also observed. But the bands which have been suggested as the most useful in the diagnostic treatment of the coordination of the bipyridyl group to a metal ion are those at 995 and 755 cm^{-1} (in free ligand). The former peak shifts to 1030 cm^{-1} in the spectrum[15] of the complex and the other (γ-CH)[16] shifts to higher frequencies, also a satellite of this band at 742 cm^{-1} (free ligand) gains

TABLE III

Assignment of the observed IR frequencies (in cm^{-1})

Compound	$\nu(O-O)$	$\nu(\overline{O-V-O})$	$\gamma(C-H)^{\alpha}$	$\gamma(C-H)^{\beta}$	$\nu(C=C)$	$\nu(C=N)$	$\nu(C-H)$
2,2 -bipyridine	—	—	755 vs 742 m	—	1455 vs	1575 vs 1550 s	3040 vs
$Li\{V(O-O)_3bipy\}.3H_2O$	900 s 878 vs	630 s	758 vs 733 m	—	1460 vs	1600 m 1570 w	3180 vs
$Ca\{V(O-O)_3bipy\}_2.2H_2O$	912 vs 858 vs	625 m	765 vs 733 s	—	1478 s	1600 vs 1580 m	3150 vs
$Ba\{V(O-O)_3bipy\}_2.2H_2O$	915 vs 860 vs	625 m 578 s	768 vs 734 s	—	1480 s	1600 vs 1585 m	3150 vs
1,10 - phenanthroline	—	—	733 vs	855 vs	1430 vs	1590 vs	3000 s
$Li\{V(O-O)_3phen\}.2H_2O$	910 s	650 m	725 vs 737 w	845 vs	1435 vs	1625 m	3450 vs
$Ca\{V(O-O)_3phen\}_2.2H_2O$	912 vs	638 m	727 vs 737 w	846 s	1435 vs	1626 m	—
$Ba\{V(O-O)_3phen\}_2.2H_2O$	912 vs	638 m	725 vs 737 w	846 s	1435 vs	1626 m	—

α ring with heteroatom
β central ring

intensity and is strongly split away [11,15] from the parent peak to 733 cm^{-1}. In addition the band at 1318 cm^{-1} may correspond to the 1320 cm^{-1} band pointed out by *Sinha*[15] for complexes with bipyridyl and rare earth elements.

Similar remarks apply to the complexes with phenanthroline. The strong bands at 733 and 855 cm^{-1} attributed to the free ligand are assigned to the hydrogen out-of-plane deformation[17]. The first band is due to the hydrogen atoms of the heteroatomic rings, while the other corresponds to those of the central ring. In the compounds, these two bands appear as doublets showing a clear splitting. In addition, a shift is observed for the bands in the 1400-1600 cm^{-1} region which are characteristics of polyheteroaromatic compounds. These facts have been mentioned by several authors[14,17] and are considered characteristic of the coordination of phenanthroline to metal through nitrogen.

The uv spectrum of 2,2 -bipyridine consists of two absorption bands at 35.7 (band I) and 42,5 kK (band II). These bands correspond essentially to $\pi \rightarrow \pi^*$ transitions[18]. The coordination of the bipyridyl to metal ions results in a red shift of the bands of the spectrum[11,19,20]. In our compounds (Table IV), the peak at 42.5 kK shows a slight red shift, while the peak at 35.7 kK shows a considerable shift and is resolved into two distinct bands at *ca.* 35.0 and 32.1 kK. These facts seem characteristic of the coordination of bipyridyl by its nitrogen atoms to vanadium.

TABLE IV

U.V. spectra (ν in kK; ε in $cm^2.mol^{-1}$)

Compounds	ν	ε	ν	ε	ν	ε
2,2 -bipyridine	42.5	16,200	35.7	21,200	—	—
$Li\{V(O — O)_3bipy\}.3H_2O$	42.6	19,400	35.0	15,600	32.1	8,800
$Ca\{V(O — O)_3bipy\}_2.2H_2O$	42.8	29,700	35.0	22,800	31.9	11,000
$Ba\{V(O — O)_3bipy\}_2.2H_2O$	42.8	32,400	35.2	25,200	31.6	12,400
1,10-phenanthroline	44.1	34,800	37.7	24,200	34.4	7,200
$Li\{V(O — O)_3phen\}.2H_2O$	44.5	40,000	37.0	28,000	33.6	8,600
$Ca\{V(O — O)_3phen\}_2.2H_2O$	44.6	44,000	36.9	29,000	33.6	9,000
$Ba\{V(O — O)_3phen\}_2.2H_2O$	—	—	36.8	33,000	33.1	13,500

In the phenanthroline complexes (Table IV) the three peaks at *ca* 33.6, 37.0 and 44.5 kK are due to the ligand itself. The ultraviolet spectrum of 1,10-phenanthroline consists of absorption maxima at 34.4, 37.7

and 44.1 kK corresponding to $\pi \rightarrow \pi^*$ transistions. The peaks at 44.1 kK and 34.4 appear slightly shifted.

The peak at 37.7 kK shows a distinct shift (*ca* 1000 cm^{-1}) comparable to the value quoted by *Bush* and *Bailar*[14] for tris (phenanthroline) iron (II) chloride. This shift seems characteristic of coordination of phenanthroline to the metal through nitrogen.

Finally, based on the spectroscopic and conductivity data given for potassium and sodium triperoxo vanadate (v) complexes coordinated to the same ligands we may suppose that our compounds should also be regarded as being eight-coordinated and that water molecules are not involved in the coordination sphere. Therefore, they may also have a distorted dodecahedral structure owing to the asymmetrical fields consisting of three bidentate peroxide groups and one bidentate nitrogen group.

BIBLIOGRAPHY

1. J. Sala - Pala, and J. E. Guerchais, J. chem. soc., sect. A, 1132, (1971).
2. C. Djordjevic, and N. Vuletic, Inorg. chem., 7, 1864 (1968).
3. M. Orhanovic, and R. G. Wilkins, J. chem. soc., 89, 278, (1967).
4. J. E. Fergusson, C. J. Wilkins, and J. F. Young, J. chem. soc., 2136, (1962).
5. R. Stomberg, Acta chem. scand., 17, 1563, (1963).
6. G. Mathern and R. Weiss, presented at the meeting of the "Societe Chimique De France", Besancon, October 1969.
7. A. I. Vogel, Quant. Inorg. Anal., 3d ed., Longmans, London, (1964).
8. W. P. Griffith, J. chem. soc., 5248, (1964).
9. O. Bain, and P. A. Gignere, Canad. J. chem. 33, 527, (1955).
10. W. P. Griffith and T. D. Wilkins, J. chem. soc., sect. A, 397, (1968), 590, (1967).
11. B. Martin, W. R. McWhinne and G. M. Waind, J. inorg. nucl. chem. 23, 207, (1961).
12. A. R. Katritzky, Quart. rev. chem. soc., 13, 375 (1959).
13. A. I. Popov, J. C. Marshall, F. B. Stute and W. B. Person, J. am. chem. soc., 83, 3586 (1961).
14. D. H. Bush and J. C. Bailar, J. am. chem. soc., 78, 1137, (1956).
15. S. P. Sinha, Spectrochim. Acta, 20, 879 (1964).
16. L. J. Bellamy, "The ir spectra of complex molecules" Methuen, London, (1964).
17. A. A. Schift and R. C. Taylor, J. inorg. nucl. chem., 9, 211, (1959).
18. A. Kiss and J. Csaszar, Acta chim. acad. sci. hung., 38, 405 and 421, (1963).
19. B. Martin and G. M. Waind, J. chem. soc., 4284 (1958).
20. K. Sone, P. Krumholz and H. Stammreich, J. am. chem. soc., 77, 777, (1955).

ΠΕΡΙΛΗΨΙΣ

ΥΠΕΡΟΞΕΙΔΙΚΑ ΣΥΜΠΛΟΚΑ ΤΟΥ ΒΑΝΑΔΙΟΥ (v)

Ὑπὸ
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Εἰς τὴν παροῦσαν ἐργασίαν ἐγένετο ἡ σύνθεσις καὶ ἡ φασματοσκοπικὴ μελέτη ὑπεροξειδικῶν συμπλόκων ἑνώσεων τοῦ πεντασθενοῦς βαναδίου μετὰ τῆς 2,2′ - διπυριδίνης καὶ τῆς 1,10 - φαινανθρολίνης. Αἱ μελετηθεῖσαι ἑνώσεις εἶναι τοῦ τύπου $M^{I}[V(O{-}O)_3(AA)]nH_2O$ καὶ $M^{II}[V(O{-}O)_3(AA)]_2nH_2O$ ὅπου $M^{I} = Li$, $M^{II} = Ca$ ἢ Ba καὶ (AA) = διπυριδίνη ἢ φαινανθρολίνη. Ἡ μέθοδος παρασκευῆς εἶναι ἰδία πρὸς τὴν χρησιμοποιηθεῖσαν διὰ τὴν παρασκευὴν ἀναλόγων ὑπεροξειδικῶν ἑνώσεων τοῦ νιοβίου (v) καὶ τοῦ ταντολίου (v)

Τὰ ληφθέντα σύμπλοκα κρυσταλλοῦνται μὲ 2 ἢ 3 μόρια ὕδατος (Πίναξ I) καὶ εἶναι μετρίως σταθερά. Προσπάθεια ἀπομονώσεως ἀνύδρων ἑνώσεων κατέληγεν εἰς διάσπασιν τῶν ἑνώσεων. Αἱ μοριακαὶ ἀγωγιμότητες (Πίναξ II) εἰς ὑδατικὰ διαλύματα ἔδειξαν ὅτι εἶναι ἠλεκτρολῦται τοῦ τύπου 1 : 1 καὶ 1 :2.

Αἱ χαρακτηριστικαὶ μετατοπίσεις ἢ διασπάσεις ὡρισμένων ζωνῶν τοῦ ὑπερύθρου φάσματος ἀποδίδονται εἰς τὸ γεγονὸς ὅτι τὰ ligands δροῦν ὡς διδόται. Τὰ φάσματα ὁρατοῦ - ὑπεριώδους τῶν συμπλόκων ἐμφανίζουν μετατοπίσεις εἰς τὰ μέγιστα ἀπορροφήσεώς των, ἐν συγκρίσει πρὸς τὰ φάσματα τῶν ἐλευθέρων ligands, ἐνδεικτικὰ τῆς συναρμογῆς τῆς διπυριδίνης καὶ τῆς φαινανθρολίνης.