Inorganica Chimica Acta, 21 (1977) 85–88

Synthesis and Properties of Oxovanadium(IV) Complexes with Schiff Bases Obtained from Pyridoxal and Various Amines

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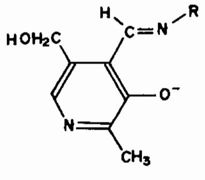
Received June 8, 1976

Oxovanadium(IV) complexes with Schiff bases obtained from pyridoxal and monoamines (RNH_2) and ethylenediamine were synthesized. The 1:2 type complexes were obtained with R = alkyl and aryl groups. They have a square-pyramidal configuration, except for the complex with $R = n - C_4H_9$, which probably has a multinuclear structure. The 1:1 type complexes were obtained with ethylenediamine and 3-hydroxypropanol for the amine component. The results are discussed in comparison with those of related salicylaldiminato complexes.

Introduction

Although extensive studies have been carried out on the interaction of metal ions with N-substituted pyridoxaldimines in solution, little work has been reported about the isolation and detailed characterization of these metal chelates. In order to obtain fundamental information from this side, we recently initiated studies on the isolation and characterization of metal complexes with Schiff bases obtained from pyridoxal. Some of the results about the cobalt, nickel and copper complexes were reported previously [1–3].

The present work is concerned with the isolation and properties of oxovanadium(IV) complexes with the Schiff bases obtained from pyridoxal and such amines as alkylamines, arylamines, n – propanolamine (I, abbreviated as pdx-R) and ethylenediamine (II, abbreviated as pdxen). Very little is known about the oxovanadium(IV) complexes with these and related ligands [4]. The results of the present work are compared with those of the salicylaldiminato complexes [5, 6].



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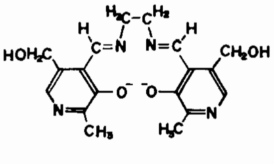

II

Experimental

Materials

Pyridoxal hydrochloride of Analar Grade was purchased from Merck and Co. and used as received.

Free pyridoxal was prepared from the hydrochloride as reported previously [3].

Oxovanadium(IV) Complexes with N-alkyl- and N-aryl-salicylaldiminates

These complexes were synthesized by the following general method. Pyridoxal (0.02 mol) and an appropriate monoamine (0.02 mol) were dissolved in ethanol and the mixture was stirred for 30 min at 60 °C, followed by addition of a solution of oxovanadium(IV) dichloride (0.01 mol) in ethanol. The resulting solution was heated at this temperature for about 3 hr and filtered. A crystalline precipitate obtained was washed with methanol containing a small amount of pyridine.

These complexes are not soluble in common organic solvents.

N-(3-Hydroxypropyl)-pyridoxaldiminato-oxovanadium(IV)

This complex was obtained as yellowish brown microcrystals by a similar method to that described above, except that the metal-to-ligand ratio was 1:1 in this case.

N,N′-Ethylene-bis(pyridoxaldiminato)-oxovanadium (IV)

This complex was synthesized as greenish brown microcrystals by a similar method to that described above.

TABLE I. Analytical Data of Oxovanadium(IV) Complexes with N-Substituted Pyridoxaldiminates.

Complex	Calcd, %			Found, %			Colour[a]
	C	H	N	C	H	N	
VO(pdx-CH_3)$_2$	50.83	5.21	13.17	50.89	5.16	13.23	yb
VO(pdx-C_2H_5)$_2$	52.98	5.78	12.36	52.83	5.77	11.88	yb
VO(pdx-n-C_3H_7)$_2$	54.89	6.28	11.64	55.43	6.33	11.70	gb
VO(pdx-iso-C_3H_7)$_2$	54.89	6.28	11.64	54.84	6.06	11.23	gb
VO(pdx-n-C_4H_9)$_2$	56.58	6.73	11.00	56.38	6.65	10.91	yb
VO(pdx-ph)$_2$	61.20	4.77	10.20	61.02	4.81	10.20	yb
VO(pdx-2,6-(CH_3)$_2$-ph)$_2$	63.47	5.66	9.25	63.46	5.52	9.14	gb
VO(pdxen)	51.05	4.76	13.24	50.36	5.03	13.22	gb
VO(pdx-$CH_2CH_2CH_2O$)	45.69	4.90	9.70	45.74	4.72	9.67	yb

[a] yb: pale yellowish–brown, gb: pale greenish–brown.

Analytical data of the oxovanadium(IV) complexes prepared in the present work are shown in Table I.

Measurements

Electronic absorption spectra were measured on a Hitachi EPS-3T spectrophotometer. Infrared absorption spectra were obtained from nujol mulls using a Hitachi EPI-G2 infrared spectrophotometer.

Magnetic measurements were carried out by the Gouy method at room temperature using CoHg(SCN)$_4$ as a calibrant.

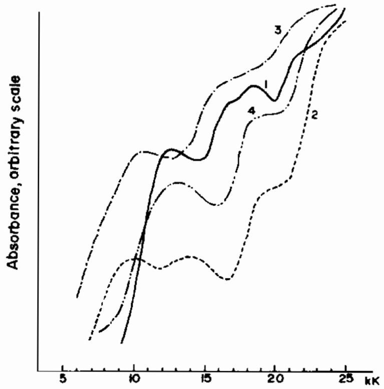

Fig. 1. Electronic absorption spectra in nujol mulls of oxovanadium(IV) complexes. 1, VO(pdx-n-C_3H_7)$_2$; 2, VO(pdx-n-C_4H_9)$_2$; 3, VO(pdxen); 4, VO(pdx-$CH_2CH_2CH_2O$).

TABLE II. Main *d–d* Band Maxima of Oxovanadium(IV) Complexes of the Type VO(pdx-R)$_2$ in Nujol Mulls.

R	ν_1[a]	ν_2	ν_3
CH_3	11.0	(16 sh)	18.7
C_2H_5	12.5	(17 sh)	18.8
n-C_3H_7	12.6	(17 sh)	18.6
iso-C_3H_7	12.6	(17 sh)	18.7
n-C_4H_9	9.6	14.1	19.6
ph	12.2	b	b
2,6-(CH_3)$_2$-ph	12 sh	b	b

[a] ν: 10^3 cm^{-1}. [b] Bands ν_2 and ν_3 are overlapped. The values in parentheses are only approximate.

Results and Discussion

Oxovanadium(IV) Complexes with Bidentate Pyridoxaldiminates

N-Alkyl- and N-aryl-pyridoxaldiminates form metal complexes of the type VO(pdx-R)$_2$. The complexes of this type, R being CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, ph and 2,6-(CH_3)$_2$-ph, exhibit three *d–d* absorption bands, as shown in Table II, where the notation ph represents phenyl nucleus. Some of the representative curves are shown in Fig. 1. Although three *d–d* bands are expected to appear, they are often overlapped over each other. Many of the absorption bands are not very sharp and it is difficult to observe distinctly all the three bands for some of the complexes. The absorption maxima lie at almost the same frequencies as those of the corresponding salicylaldiminato-complexes. It may be reasonable to assume that they all should have an essentially square-pyramidal configuration [5, 6]. It is found that steric hindrance against the square-pyramidal configuration in VO(pdx-iso-C_3H_7)$_2$ and VO(pdx-2,6-(CH_3)$_2$-ph)$_2$ is not large enough to exclude this configuration.

Fig. 1 and Table II show that the complex VO(pdx-n-C_4H_9)$_2$ has an absorption spectrum which is remarkably different from those of the other N-alkyl analogues and the N-n-butylsalicylaldiminato complex [5]. This finding indicates that VO(pdx-n-C_4H_9)$_2$ may have a structure different from that of the other N-alkyl analogues. The magnetic moment (1.54 BM) at room temperature of VO(pdx-n-C_4H_9)$_2$ is much smaller than the normal magnetic moment of the d^1 system. A sort of interaction therefore, is expected to exist between vanadium(IV) ions in this

TABLE III. Infrared ν(V=O) Band Maxima of Oxovanadium (IV) Complexes with N-Substituted Pyridoxaldiminates, VO(pdx-R)$_2$, and Salicylaldiminates, VO(Sal-R)$_2$.

R	VO(pdx-R)$_2$	VO(sal-R)$_2$
CH_3	963[a]	970
C_2H_5	985	973
n-C_3H_7	990	975
iso-C_3H_7	990	969
n-C_4H_9	898	968
ph	983	976
2,6-$(CH_3)_2$-ph	995	972

[a] ν(V=O): cm^{-1}.

complex. Moreover, its infrared ν(V–O) band (898 cm^{-1}) is found to be enormously lower than those of the other N-alkyl analogues (Table III). On the basis of the previously proposed criterion that the anomalously low V=O stretching frequency is diagnostic of a multinuclear structure *via* V–O–V interaction [7], it is most likely that VO(pdx-n-C_4H_9)$_2$ may have a multinuclear structure with axial V–O–V bridges.

It may be worth mentioning that VO(pdx-CH_3)$_2$ shows the first *d–d* band at a significantly lower frequency (10.9 kK), as compared with those of the other N-alkyl analogues. Its V=O stretching frequency (963 cm^{-1}) is also lower, though slightly, than the normal frequencies (985–995 cm^{-1}), as may be seen in Table III. Its magnetic moment at room temperature (1.85 BM), however, is considered to be normal for the d^1 system [8]. Its structure, therefore, may not be fundamentally different from that of the N-ethyl- or N-n-propyl- analogue, but may be a structure distorted to some extent from that of the N-ethylanalogue. A binuclear structure possibly with phenolic oxygen atom as a bridge cannot be excluded.

As may be seen in Table III, the V=O stretching frequencies of the pyridoxaldiminato complexes are higher than those of the corresponding salicylaldiminato complexes, a fact which probably shows that the axial V=O bond order in the former complexes may be higher than that in the latter complexes. It was assumed previously that the greater the donation of ligand electrons to vanadium(IV) ion, the greater would be the decrease expected in the V–O stretching frequency [9]. If this assumption is correct, the present data seem to indicate that the in-plane ligand-to-metal bond in the pyridoxaldiminato complexes may be weaker than in the salicylaldiminato complexes.

There is another significant difference in the infrared spectra between the pyridoxaldiminato and salicylaldiminato complexes. The latter complexes show a characteristic band in the region between 1500 cm^{-1} and 1560 cm^{-1}, while the former have no band in this region. This finding seems to give a hint as to the assignment of this infrared band. Thus the current assignment of this band to C–O(phenolic) vibration probably needs reconsideration.

Oxovanadium(IV) Complexes with Terdentate and Quadridentate Pyridoxaldiminates.

As shown in Fig. 1, the electronic absorption spectrum of VO(pdxen) is very different from those of the N-alkylpyridoxaldiminates. Furthermore, its infrared V=O stretching vibration (868 cm^{-1}) appears at a much lower frequency than those of the other oxovanadium(IV) complexes having a square-pyramidal configuration. As discussed in the preceding paragraph of the present paper, the very low V=O frequency implies that VO(pdxen) may have a multinuclear structure *via* V–O–V bridges. In this respect, this complex is similar to VO(salpn), where salpn denotes N, N′-1-methylethylenebis (salicylaldiminate). The latter complex also shows a very low V=O frequency (854 cm^{-1}) and was concluded from X-ray studies to have a multinuclear structure with V–O–V bridges [10]. It is very likely that VO(pdxen) has a similar structure to that of VO (salpn). The magnetic moment at room temperature (1.53 BM) is found to be significantly lower than the normal moment for the d^1 system, probably showing that there is spin–spin interaction between vanadium (IV) ions through an oxygen atom in this complex.

The magnetic moment (1.28 BM) of VO(pdx-$CH_2CH_2CH_2O$) is much lower than the normal moment for the d^1 system. A sort of exchange interaction seems to exist between vanadium(IV) ions in this complex, as in the analogous salicylaldiminato complexes [11, 12]. It is most probable that VO($CH_2CH_2CH_2O$) has a multinuclear, possibly binuclear, structure similar to that of the corresponding salicylaldiminato complexes.

Acknowledgment

The present authors wish to thank Mr. Hiro Kuma for helpful discussion.

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