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THE REACTION OF TRICHLOROOXOVANADIUM(V) WITH SOME OXYGEN DONOR LIGANDS

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Summary

The β-diketone complexes of chlorooxovanadium(V) of the type $VOCl(dik)_2$ (where dik ≡ btfac, bzac and ttfac) were prepared by the reaction of $VOCl_3$ with the appropriate ligand in dry toluene under anhydrous conditions. $VOCl_3 \cdot Ph_3PO$ was also prepared by the reaction of $VOCl_3$ with Ph_3PO in dichloromethane. These complexes were characterized by analysis, melting point measurements, IR and Raman spectra, nuclear magnetic resonance (NMR), mass spectral studies and X-ray powder diffraction.

1. Introduction

We report the preparation of $VOCl(dik)_2$ (where dik ≡ btfac, bzac and ttfac) by the reaction of trichlorooxovanadium(V) with the appropriate ligand in toluene in a dinitrogen atmosphere. The reaction of $VOCl_3$ with triphenylphosphine oxide results in the formation of $VOCl_3 \cdot Ph_3PO$.

The reaction of trichlorooxovanadium(V) with a number of monodentate oxygen and nitrogen donor ligands (L) and bidentate ligands (B) results in the formation of $VOCl_3 \cdot 2L$ and $VOCl_3 \cdot B$ respectively [1 - 3]. $VOCl_4^-$ complexes may also be formed by the reaction of V_2O_5 or $VOCl_3$ with chlorinating agents [4]. The reaction of $VOBr_3$ with a number of monodentate ligands and some bidentate ligands results in the reduction of $VOBr_3$ and gives rise to dibromooxovanadium(IV) complexes of the types $VOBr_3^-$, $VOBr_4^{2-}$, $VOBr_5^{3-}$, $VOBr_2 \cdot 2L$, $VOBr_2L_3$, $VOBr_2L_5$ and $VOBr_2$(L—L) [5, 6].

Although a large number of β-diketonate complexes of oxovanadium(IV) have been extensively studied [7 - 17], relatively few reports have been published about oxovanadium(V) complexes with chelating ligands. Funk *et al.* [13] in 1958 reported the preparation and characterization of VOCl(acac)$_2$ and VOCl (diacetyldioxime). Fackler *et al.* [18] also reported the

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synthesis of a number of $VOCl(dik)_2$ (where dik ≡ acac, tfac, hfac, bzbz) from the reaction of $VOCl_3$ with diketone.

Recently, it has been reported that the reaction of trichlorooxovanadium(V) with dipicolinic acid as a primary ligand and several nitrogen and oxygen containing donor molecules as secondary ligands results in the formation of mixed ligand complexes of oxovanadium(V) with complete chloride substitution [19].

2. Experimental details

All reactions were handled in a dry-box filled with oxygen-free dinitrogen.

2.1. *Material*

$VOCl_3$ (Alfa), Ph_3PO (BDH), $C_6H_5COCH_2COCF_3$ (Aldrich), C_6H_5-$COCH_2COCH_3$ (BDH), $C_4H_3SCOCH_2COCF_3$ (BDH), CH_2Cl_2 (BDH), C_6H_5-CH_3 (BDH) were purified and dried by standard methods.

2.2. *Analytical determination*

Analysis of vanadium, chlorine, phosphorus, sulphur, carbon and hydrogen was carried out in the Microanalytical Laboratory, Chemistry Department, Manchester University by Mr. M. Hart.

2.3. *Preparation of compounds*

2.3.1. *Preparation of $VOCl_3 \cdot Ph_3PO$*

Ph_3PO was dissolved in dichloromethane and the stoichiometric amount (1:1 mol ratio) of $VOCl_3$ was added dropwise with continuous agitation under anhydrous conditions. The reaction was exothermic and the resulting reddish-brown solution was concentrated to one-quarter of its original volume and left in a refrigerator for two days by which time some brown precipitate was formed. $VOCl_3 \cdot Ph_3PO$ requires V, 11.29%; Cl, 23.58%; C, 47.8%; H, 3.39%; P, 6.86%. Analysis found was V, 10.7%, Cl, 23.7%; C, 47.2%; H, 3.3%; P, 7.2%.

2.3.2. *Preparation of $VOCl(dik)_2$*

The appropriate diketone was dissolved in toluene or benzene and the stoichiometric amount (2:1 mol ratio) of $VOCl_3$ was added dropwise with continuous agitation under anhydrous conditions. The resulting black solution was concentrated to half of its original volume and left overnight, by which time some greenish-black precipitate was formed.

$VOCl(btfac)_2$ requires V, 9.58%; Cl, 6.66%; F, 21.40%; C, 45.07%; H, 2.25%. Analysis found was V, 9.2%; Cl, 6.8%; F, 20.85%; C, 44.5%; H, 2.5%. Melting point was 130 °C, decomposition.

$VOCl(bzac)_2$ requires V, 12.07%; Cl, 8.40%; C, 56.80%; H, 3.78%. Analysis found was V, 11.25%; Cl, 8.8%; C, 55.8%; H, 4.0%. Melting point was 112 °C, decomposition.

$VOCl(ttfac)_2$ requires V, 9.36%; Cl, 6.52%; F, 20.93%; S, 11.75%; C, 35.26%; H, 1.47%. Analysis found was V, 8.75%; Cl, 5.8%; F, 21.35%; S, 11.8%; C, 38.1%; H, 1.8%.

2.4. Physical measurements

2.4.1. IR specta

IR spectra were recorded using a Perkin–Elmer 557 (4000 - 200 cm^{-1}) instrument. Nujol mulls were prepared in a dry-box.

2.4.2. Raman spectra

Raman spectra of powdered samples were recorded using a Spex 1403 double spectrophotometer instrument. Samples were prepared in a dry-box.

2.4.3. X-Ray powder photographs

Photographs were obtained using a Debye–Scherrer camera with a diameter of 5.37 cm. In all cases Cu Kα radiation was used.

2.4.4. Mass spectral measurements

Mass spectra of some of the complexes were recorded on an AEI 12 mass spectrometer at a nominal 70 eV excitation.

3. Results and discussion

Trichlorooxovanadium(V) reacts with Ph_3PO and diketone at room temperature in dichloromethane and toluene to form $VOCl_3 \cdot Ph_3PO$ and VOCl(dik) where dik ≡ bzac, btfac and ttfac. These complexes are moisture sensitive and soluble in common organic solvents. The phosphine oxide complex is more stable than the β-diketonate complexes and shows no visible sign of decomposition on exposure to air for several hours.

IR spectra provide valuable information regarding the nature of the carbonyl group attached to the metal atoms. In addition, evidence for the quasi-aromatic behaviour of the six-membered chelate ring and the structural features of metal β-diketonate derivatives has also been adduced in some cases from these studies. The assignments that are important from the above points of view are those for ν(C═O), ν(C═C) and ν(M═O).

Liang *et al.* [20] studied the IR spectra of a variety of complexes of β-diketonates of europium(III). These workers also supported the corrected assignments of Pinchas *et al.* [21] and those of Behnke and Nakamoto [22, 23], and the bands at 1600 and 1515 cm^{-1} observed for $Eu(acac)_2 \cdot 2H_2O$ were assigned to C═O and C═C stretching modes respectively. It was also observed that the replacement of methyl by trifluoromethyl strengthened the C═O and C═C bonds and weakened the M—O bonds. The former two bands were therefore shifted to higher frequencies and the latter to lower frequencies. This observation is in agreement with those made earlier by Nakamoto *et al.* [24]. They carried out the IR spectra studies of acetylacetonates and trifluoro- and hexafluoro-acetylacetonates of nickel and copper. They observed that successive replacement of methyl groups by trifluoromethyl groups caused a shift of C=O and C=C stretching frequencies to higher regions and the corresponding M—O band to a lower region. This observation was in agreement with the electronic theory of bonding, according to which the strong negative inductive effect of a CF_3 group strengthens the C=O and C=C bonds and weakens M—O bonds. It was also observed that the replacement of methyl or trifluoromethyl by a phenyl group caused a shift of C=C and M=O bands to higher regions, but the shift of the C=O band was somewhat irregular. In order to get evidence for this, Nakamoto *et al.* [24] carried out perturbation calculations for dibenzoylmethanates of copper and nickel and found that the phenyl substitution slightly increased the C=C and M—O stretching force constants and slightly decreased the C=O stretching force constant. Taking into account the mesomeric interaction of the phenyl group with the quasi-aromatic metal chelate ring, the resonance shift of π electrons to the chelate ring can be assumed from the resonance forms depicted in Fig. 1. These structures indicate that, as a result of the mesomeric effect by the phenyl group, the negative charge on the oxygen atom increases, bringing about a strengthening in the σ as well as to some extent the π character of the M—O bond.

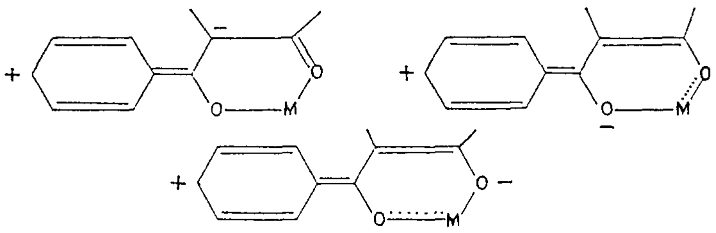

Fig. 1. Resonance forms in metal chelate ring.

The recorded spectra of $VOCl(bzac)_2$ and $VOCl(btfac)_2$ showed strong absorptions at (1590, 1520) cm^{-1} and (1624, 1570) cm^{-1} which are assigned to ν(C=O) and ν(C=C) stretching vibrations respectively and they are in good agreement with the above discussion.

Brown *et al.* [25] have reported that the lowering of the ν(P=O) vibration on coordination occurs in agreement with a decrease in the bond order, probably owing to a decrease in P_π–d_π bonding. The recorded IR spectrum of Ph_3PO shows a strong absorption at 1195 cm^{-1} which is assigned to the ν(P=O) stretching vibration. Upon coordination this is shifted to 1050 cm^{-1}, with a lowering of 145 cm^{-1} for $VOCl_3 \cdot Ph_3PO$. The strong absorption at 372 cm^{-1} in the IR and 370 cm^{-1} in the Raman spectra of $VOCl_3Ph_3PO$, at 363 cm^{-1} in the IR and 335 cm^{-1} in the Raman spectra of $VOCl(btfac)_2$ and 359 cm^{-1} in the IR spectrum of VOCl(bzac) are assigned to the ν(V—Cl) stretching vibration. The strong absorption at 1020 cm^{-1} in the IR spectrum of $VOCl_3 \cdot Ph_3PO$, at 1002 cm^{-1} in the IR and 997 cm^{-1} in the Raman spectra of $VOCl(bzac)_2$ and at 980 cm^{-1} in the IR and 899 cm^{-1} in the Raman spectra of $VOCl(btfac)_2$ are assigned to ν(V=O) stretching vibrations.

The NMR spectrum of benzoyltrifluoroacetone has δ 15.15 broad singlet (1H, enol form); 8.02 doublet (2H, ortho); 7.68 triplet (1H, para); 7.56 triplet (2H, meta) and 6.64 singlet (1H, olefin), which upon coordination is shifted to (6.9 - 8.45) multiple with fine structure for phenyl protons and no signal is observed for low field enol and olefin protons. The NMR spectrum of benzoylacetone showed δ at 16.23 singlet (1H, enol form); 7.96 doublet with fine structure (2H, Ph); (7.50 - 7.62) multiple with fine structure (3H, protons); 6.22 singlet (1H olefin) and 2.18 singlet (3H, Me) which upon coordination is shifted to (7.12 - 7.76) multiple with fine structure for phenyl protons and 2.34 singlet (3H, Me) and there is no sign of enol and olefin protons.

Triphenylphosphine oxide has δ (CD_2H_2, 300 MHz) 6.2 - 6.45 multiple for the phenyl proton which upon coordination to $VOCl_3$ is shifted to 6.3 - 6.55 multiple. The NMR resonance of the complexed ligand is at a lower field than the free ligand, indicating a decrease of electron density on the proton owing to coordination.

The electron spin resonance measurements on solid $VOCl_3 \cdot Ph_3PO$ indicated no signal and this is compatible with the 5+ oxidation state for vanadium where the electron configuration is formally d^0.

In metal β-diketonates in which coordination to metals occurs via the oxygen atom, the chelate ring is planar and the π electron density is partially delocalized over the chelate ring. From the mass spectra studies of metal acetylacetonates McDonald and Shannon [26] postulated valency changes in the metal to account for the observed mass spectra of several acetylacetonates, and correlated these with the occurrence or non-occurrence of valency changes within the established chemistry of the metal. Bancroft *et al.* [27] have discussed the results of mass spectral studies and concluded that they are consistent with the loss of an electron from an orbital localized mainly on the ligand. Changes in the appearance potentials for a number of substituted acetylacetonates could be correlated with the bonding properties of various substituents to a ring which has aromatic character. The peaks observed in mass spectral studies of chlorooxovanadium(V) β-diketonates represent fragments which include loss of chlorine, one complete ligand, two complete ligands or loss of an α or γ group on the carbon ring. The mass spectral studies of $VOCl(dik)_2$ show the following mass peaks: (i) $VOCl(btfac)_2$: $VO^{35}Cl(OCPhCHCF_3CO)_2$, 532(0.1); $VO(OCPhCHCF_3CO)_2$, 497(39.0); $VO(OCPhCHCF_3CO)(OCPhCHCO)$, 428(1.7); $VO(OCPhCF_3CO)(OO)$; $VO(OCPhC)_2$, 301(19.2); $VO(OCPhCHCF_3CO)$; $VO(OCPhCHCO)(OCCHCO)$, 282(5.1); $VO(OCPhO)(OCO)$, 232(10); $VO(OCPhC)(OC)$, 212(6.3); $VO(OCPh)(O)$, 188(4.1); $VO(OCCCHCHO)$, 149(10.4); VO, 67(1.2); V, 51(7.4); (ii) $VOCl(bzac)_2$: $VO^{35}Cl(OCPhCHMeCO)_2$, 424(0.1); $VOCl(OCPhCHMeCO)(OCPhCMeCO)$, 423(0.8); $VO(OCPhCHMeCO)_2$, 389(35.5); $V(OCPhCHMeCO)_2$, 373(1.6); $V(OCPhCHMeCO)_3$, 534(0.8); $VOCl(OCPhCO)(OCCCO)$, 303(11.1); $VOCl(OCMeCHO)(OCMeC)$, 245(15); $VO(OCPhCHMeCO)$, 228(16.4); $VO(OCMeCCO)$, 150(7.9); VO, 67(7.4); V, 51(20.1).

TABLE 1

X-ray powder diffraction of trichlorooxovanadium(V) complexes

$VOCl_3 \cdot Ph_3PO$		$VOCl(btfac)_2$		$VOCl(bcaz)$	
d (Å)	Intensity	*d* (Å)	Intensity	*d* (Å)	Intensity
9.36	m	9.35	s	11.33	s
7.25	s	8.12	w	9.12	s
6.65	vs	6.84	w	7.69	m
5.70	m	6.44	w	6.86	m
5.02	w	5.18	m	6.39	w
4.62	m	5.10	w	6.01	w
4.17	s	4.85	m	5.39	s
3.92	m	4.65	w	4.87	s
3.48	w	4.42	s	4.60	m
3.27	vw	4.17	vw	4.43	m
3.11	vw	3.91	m	4.15	w
2.93	w	3.79	vw	3.85	w
2.82	vw	3.60	w	3.55	s
2.75	vw	3.47	m	3.46	m
2.26	vw	3.38	w	3.34	m
2.51	vw	3.21	w	3.27	w
2.42	w	3.14	w	3.08	vw
2.32	vw	2.69	vw	2.97	w
		2.61	vw	2.81	vw
		2.43	vw	2.69	vw
		2.35	vw	2.61	vw
		2.26	vw	2.30	w
		2.19	vw	2.21	vw
				2.03	vw
				1.99	w

s, strong; m, medium; w, weak; v, very.

The X-ray powder diffraction results for complexes prepared in this study are listed in Table 1. The compounds appear to possess low symmetry, but the results have not been interpreted in detail.

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