Studies on Metal Carboxylates. VIII.[1] Reactions of Acetylacetonates of the First Row Transition Elements with Pyridine-2,6-dicarboxylic Acid[a]

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The acetylacetonates $VO(acac)_2$, $M(acac)_3$, where $M = V$, Mn or Fe and $[M'(acac)_2]_n$, where $M' = Co$, Ni or Cu, have been reacted with pyridine-2,6-dicarboxylic acid ($dipicH_2$) in acetone to afford the complexes $VO(dipic) \cdot 2H_2O$, $M(acac)(dipic) \cdot xH_2O$ [$M = V$, Mn or Fe and $x = 1$ or 0] and $M_2(dipic)$ $(dipicH)_2 \cdot yH_2O$ [$M = Co$, Ni or Cu and $y = 2$ or 0]. The cobalt(II) and nickel(II) complexes are converted to polymeric $[M(dipic)]_n$ in ethanol and all three complexes formulated as $M_2(dipic)(dipicH)_2$ react with 2,2',2''-terpyridyl to yield $M(dipic)(terpy) \cdot 3H_2O$. The vanadium(III) complex $V(acac)(dipic)$ is oxidized to $VO(dipic) \cdot 4H_2O$ in aqueous solution via the vanadium(III) intermediate $V(OH)(dipic) \cdot 2H_2O$. Tentative structural conclusions are drawn for certain of these new complexes based upon room temperature spectral and magnetic measurements. The characterization of these complexes has included selected studies of their X-ray photoelectron spectra.

Introduction

We have previously observed[3] that the reaction of cobalt(II) acetylacetonate $[Co(acac)_2]_4$ with pyridine-2,6-dipicolinic acid ($dipicH_2$) affords the unusual polymeric complex $[Co(dipic)]_n$. This species reacts with water, pyridine and α-picoline to afford six coordinate derivatives of the type $Co(dipic)(L)_3$. The synthesis of $[Co(dipic)]_n$ suggested that related derivatives of other transition metals might also be accessible by such a route, and since we suspected that such species might exhibit a varied chemistry, we have explored the reactions of a variety of acetylacetonates of the first-transition series with pyridine-2,6-dicarboxylic acid. The results of this study are now reported.

Experimental

Starting Materials

The ligands and solvents used in this study were obtained from commercial sources and were used as received except unless otherwise stated. Pyridine-2,6-dicarboxylic acid (dipicolinic acid), abbreviated $dipicH_2$, was obtained from the Aldrich Chemical Company and acetylacetone, abbreviated acacH, from Matheson, Coleman and Bell.

$V(acac)_3$ was prepared by the procedure of Grendić and Korpar–Čolig[4] from the zinc reduction of VO $(acac)_2$ in freshly distilled dry acetylacetone. The crude brown crystalline product was purified by recrystallization from dry diethyl ether and sublimation *in vacuo*.

The starting materials $[Ni(acac)_2]_3$ and $Cu(acac)_2$ were prepared by standard literature methods[5], while samples of the complexes $[Co(acac)_2]_4$, $Mn(acac)_3$ and $Fe(acac)_3$ were available from existing sources within this laboratory. Their identity was confirmed by infrared spectroscopy.

Reaction of Metal Acetylacetonates with Pyridine-2,6-dicarboxylic Acid

$V(acac)_3$

$V(acac)_3$ (0.21 g) was dissolved in 5 ml dry deoxygenated acetone (spectra grade) and mixed with a solution of $dipicH_2$ (0.20 g) in 40 ml acetone. The reaction mixture was then refluxed under nitrogen for 10 minutes whereupon a mustard yellow-to-brown colored solid precipitated from the hot solution. The precipitate was allowed to settle, the supernatent solution removed using a syringe and the remaining solid dried in a flow of nitrogen. Yield, 60%. This complex is sensitive to oxygen and moisture and consequently, it was handled in a dry nitrogen atmosphere during its characterization. It does not sublime *in vacuo* and appears to be thermally stable to at least 200°C.

It is insoluble in hydrocarbon and chlorocarbon solvents but is soluble to some degree in polar solvents such as methanol, ethanol, tetrahydrofuran, acetone, dimethylsulfoxide, acetonitrile, dimethylformamide and pyridine. Immediate reaction occurs when this complex is reacted with water as described below.

(a) V(acac)(dipic)(~1 g) was added to 25–30 ml ice water, the reaction flask sealed and the reaction mixture stirred for 30 minutes. The bright yellow insoluble product, which appears to have a stoichiometry close to $V(OH)(dipic) \cdot 2H_2O$ (Table I), was filtered off, washed with small portions of acetone and diethyl ether and dried *in vacuo* for no more than 15 minutes. Further pumping results in partial dehydration to the monohydrate $V(OH)(dipic) \cdot H_2O$. *Anal.* Calcd. for $V(OH)(dipic) \cdot H_2O$: C, 33.5; H, 2,4; N, 5.6. Found: C, 33.8; H, 3.5; N, 5.5. This material exhibited similar electronic and infrared spectra, except for changes in the $\nu(OH)$ region, to that of the dihydrate (see Results and Discussion) so its characterization was not pursued further.

(b) When V(acac)(dipic) was treated with warm water it dissolved to form a yellow solution which soon turned green. This solution was concentrated by evaporation to low volume (~10 ml) by heating at $100\degree C$, by which time it had turned an intense blue, and it was then maintained at room temperature for four days to afford a crop of brilliant blue-green crystals of VO(dipic)·$4H_2O$ (Table I). When this tetrahydrate was pumped *in vacuo* at room temperature it was converted to the blue-grey dihydrate within 20 hours, a change which occurred at a much slower rate at atmospheric pressure.

VO(acac)₂

The reaction of equimolar quantities of $VO(acac)_2$ and pyridine-2,6-dicarboxylic acid in hot acetone, without any special precautions to ensure the complete absence of moisture, afforded the insoluble blue-grey complex $VO(dipic) \cdot 2H_2O$ (Table I), identical to that obtained from the partial dehydration of VO(dipic)·$4H_2O$. This product was separated from the reaction mixture by centrifugation.

The treatment of VO(dipic)·$2H_2O$ with equimolar proportions of 2,2'-bipyridyl (bipy) or 1:10-phenanthroline (phen) monohydrate in refluxing ethanol or mixed ethanol-benzene, both solvent systems containing a few drops of triethylorthoformate,[6] afforded brown crystals of the complexes VO(dipic)(bipy) and VO(dipic)(phen)·$^1/_2 H_2O$, respectively, in 50–60% yield (Table I). Similar 1:1 complexes with bipy and phen have previously been isolated by others[7] as the monohydrates.

Mn(acac)₃

A dark red-brown product of stoichiometry close to Mn(acac)(dipic)·H_2O precipitated on reacting Mn(acac)₃ with pyridine-2,6-dicarboxylic acid in dry deoxygenated acetone, using a procedure similar to that already described for the analogous vanadium reaction. Yield ~60%. This material was insoluble in non-polar solvents and was decomposed by polar solvents in which it dissolved. It decomposed in air but was stable for a short period when kept in a N_2 atmosphere.

Fe(acac)₃

The red-brown crystalline complex Fe(acac)(dipic) (Table I) was obtained in 93% yield by the reaction of Fe(acac)₃ (2.0 g) with pyridine-2,6-dicarboxylic acid (2.0 g) in 200 ml undried reagent grade acetone. This complex is stable in air and exhibits similar solubility patterns to its vanadium analogue.

When this reaction was carried out in refluxing methanol or ethanol and the resulting dark red reaction evaporated in air, dark red crystals of Fe(acac)(dipic)·H_2O (Table I) were formed.

[Co(acac)₂]₄

The reaction between $[Co(acac)_2]_4$ (0.26 g) and pyridine-2,6-dicarboxylic acid (0.33 g) in 60 ml deoxygenated acetone afforded a light-purple complex of stoichiometry $Co_2(dipic)(dipicH)_2 \cdot 2H_2O$ in quantitative yield (Table I). This product was separated from the clear colorless filtrate, washed with 3×5 ml portions of diethyl ether, dried under reduced pressure and stored *in vacuo* over $CaSO_4$. The two water molecules associated with this complex are retained up to at least $140\degree C$ *in vacuo*.

Addition of the above complex to refluxing ethanol or 1,4-dioxane afforded the insoluble polymer $[Co(dipic)]_n$ in quantitative yield, a complex which we had previously[3] isolated from the reaction between $[Co(acac)_2]_4$ and pyridine-2,6-dicarboxylic acid in ethanol. The complex $Co_2(dipic)(dipicH)_2 \cdot 2H_2O$ dissolved with heating in anhydrous methanol. Evaporation of the solvent afforded a pink residue which we were unable to characterize adequately since it rapidly began to convert to the bright purple complex $[Co(dipic)]_n$, a change which was complete at $100\degree C$ in vacuo. It is probably a methanol complex such as $Co(dipic)(MeOH)_3$ (i.r. spectrum), analogous to the unstable pyridine complex $Co(dipic)(py)_3$,[3] which also converts to $[Co(dipic)]_n$ at $100\degree$ *in vacuo*.

When $Co_2(dipic)(dipicH)_2 \cdot 2H_2O$ (0.037 g) was added to a mixed benzene (1 ml)–acetone (20 ml) solution of 2,2',2''-terpyridyl (0.026 g), and the reaction mixture stirred for 15 minutes, the dark brown complex $Co(dipic)(terpy) \cdot 3H_2O$ was formed (Table I). This product (0.039 g) was filtered off, washed with diethyl ether and dried under reduced pressure.

[Ni(acac)₂]₃

The anhydrous lime green complex $Ni_2(dipic)(dipicH)_2$ was prepared in quantitative yield by a procedure analogous to that described above for the related cobalt(II) complex.

On one occasion, treatment of this complex for 24 hours with refluxing ethanol, containing a few drops of triethylorthoformate, produced the 1:1 complex $[Ni(dipic)]_n$. For reasons which are not yet clear, we have been unable to repeat this preparation.

The reaction of $Ni_2(dipic)(dipicH)_2$ (0.033 g) with 2,2',2''-terpyridyl (0.023 g) in a mixed benzene

TABLE I. Analytical Data and Magnetic Properties for Complexes of Pyridine-2,6-Dicarboxylic Acid.

Starting Acetylacetonate	Reaction Product	%C Calcd.	Found	%H Calcd.	Found	%N Calcd.	Found	μ_{eff}(B.M.), 298°K
V(acac)₃	V(acac)(dipic)ᵃ	45.7	45.8	3.2	3.4	4.4	4.2	2.73
	V(OH)(dipic)·2H₂O	31.2	30.5	3.0	3.9	5.2	5.0	2.45
	VO(dipic)·4H₂O	27.6	27.7	3.6	3.6	4.6	4.4	–
VO(acac)₂	VO(dipic)·2H₂O	31.4	31.1	2.6	3.0	5.2	5.0	–
	VO(dipic)(bipy)	52.6	52.6	2.9	2.9	10.8	10.6	–
	VO(dipic)(phen)·¹/₂H₂O	54.2	54.1	2.9	3.1	10.0	9.8	–
Mn(acac)₃	Mn(acac)(dipic)·H₂Oᵇ	42.7	42.9	3.6	3.5	4.1(5)	4.3	4.63
Fe(acac)₃	Fe(acac)(dipic)	45.0	45.1	3.1(5)	3.3	4.4	4.3	5.95
	Fe(acac)(dipic)·H₂O	42.6	42.5	3.6	4.2	4.1	4.1	–
[Co(acac)₂]₄	Co₂(dipic)(dipicH)₂·2H₂O	38.7	38.8	2.3	2.4	6.4(5)	6.5	4.85
	Co(dipic)(terpy)·3H₂O	51.7	51.5	3.9	3.1	11.0	10.6	–
[Ni(acac)₂]₃	Ni₂(dipic)(dipicH)₂	41.0	41.2	1.8	2.1	6.8	6.7	2.85
	[Ni(dipic)]ₙ	37.6	37.4	1.3(5)	1.6	6.3	6.5	–
	Ni(dipic)(terpy)·3H₂O	51.7	51.4	3.9	3.7	11.0	10.6	–
Cu(acac)₂	Cu₂(dipic)(DipicH)₂	40.4	40.7	1.8	2.2	6.7	6.6	1.93
	Cu₂(dipic)(dipicH)₂·EtOH	41.2	41.1	2.6	2.9	6.3	6.5	–
	Cu(dipic)(terpy)·3H₂O	51.2	51.0	3.9	3.8	10.9	10.6	–

ᵃ V analysis: Calcd., 16.2; *Found*, 16.0. ᵇ Mn analysis: Calcd., 16.3; *Found*, 15.6.

(1 ml)–acetone (14 ml)–methanol (10 ml) solvent gave a green solution which was concentrated by distillation *in vacuo*. The resulting solution was maintained at *ca.* 5°C for 3 hours to yield 0.017 g of the beige colored complex Ni(dipic)(terpy)·3H₂O (Table I).

When the complexes Ni₂(dipic)(dipicH)₂ and [Ni(dipic)]ₙ were dissolved in water and the resulting green solutions concentrated, crystals of the known complexes Ni(dipicH)₂·3H₂O and Ni(dipic)·3H₂O³, were produced.

Cu(acac)₂

The blue complexes Cu₂(dipic)(dipicH)₂ (95% yield) and Cu(dipic)(terpy)·3H₂O were formed by analogous reactions to those described for [Co(acac)₂]₄ and [Ni(acac)₂]₃, respectively. An important modification in the synthesis of Cu₂(dipic)(dipicH)₂ involved a one hour reflux of the reaction mixture followed by extraction of the insoluble product with chloroform to remove any unreacted Cu(acac)₂.

When Cu₂(dipic)(dipicH)₂ was dissolved in ethanol or Cu(acac)₂ reacted with pyridine-2,6-dicarboxylic acid in this same solvent, a turquoise product of stoichiometry Cu₂(dipic)(dipicH)₂·EtOH was produced when the solution was concentrated and then cooled to *ca.* 5°C.

Physical Measurements

These were carried out as described in Parts III and IV of this series.[3,8]

Results and Discussion

M(acac)₃

The reactions of V(acac)₃ and Fe(acac)₃ with acetone solutions of pyridine-2,6-dicarboxylic acid (dipicH₂) afforded analytically pure complexes of stoichiometry M(acac)(dipic). The room-temperature magnetic moments of these complexes, 2.73 and 5.95 B.M. respectively, confirm that the oxidation states of the parent tris-acetylacetonates are preserved.

Although both complexes are soluble in polar solvents (*e.g.* DMF, DMSO and pyridine), evaporation of these solutions to dryness did not afford the unchanged starting materials neither did it yield pure adducts of the type M(acac)(dipic)L. Thus, when the brown solution resulting from the dissolution of Fe(acac)(dipic) in pyridine was evaporated, the resulting residue was found to have a composition (C, H and N microanalyses) close to Fe(acac)(dipic)(py)₀.₇₅, consistent with the partial loss of pyridine from the 1:1 adduct. Solutions of these two complexes in DMF, DMSO and

pyridine were essentially non-conducting, so that nei-ther species possesses an ionic structure. Infrared spec-tral measurements clearly showed the presence of the coordinated acetylacetonato[9] and pyridine-2,6-dicarb-oxylato[10] moieties. Selected frequencies which are diag-nostic of ν(COO) of coordinated dipic and "ν(O ⸺ O)" of coordinated acac are given in Table II. While the infrared spectra of these two complexes are very similar, they are by no means identical, a strong indication that they do not possess the same structure. This conclusion is further supported by X-ray powder measurements which clearly show that the vanadium and iron com-plexes are not isomorphous. Neither complex contains coordinated or 'lattice' water and the vanadium(III) complex is not contaminated with any vanadyl impurity.

In the solid-state, these complexes can reasonably be expected to be either five-coordinate monomers or six coordinate dimers, with dipic or acac bridges.[11, 12] Un-fortunately, there are few five-coordinate complexes of these two oxidation states which are known and none which possess a comparable ligand arrangement to that obtained in the present work to enable us to make meaningful spectral comparisons. However, it is clear that the vanadium(III) spectrum does not correspond to that expected for a trigonal bipyramidal geometry.[13]

The solid and solution spectra of V(acac)(dipic) re-semble the general spectral features reported for V (acac)$_3$,[14, 15] namely a weak absorption between $\sim$ 16,000 and $\sim$ 18,000 cm^{-1} [observed at 16,400 cm^{-1} in the spectrum of V(acac)(dipic)] and the onset of fairly intense charge transfer bands above 20,000 cm^{-1} which obscure any high energy d$\leftrightarrow$d transitions. The low energy absorption band at 16,400 cm^{-1} can, by com-parison with the electronic absorption spectra of other octahedral vanadium(III) complexes,[16] be assigned to the $^3T_{1g}(F)\rightarrow{}^3T_{2g}(F)$ ligand field transition. While the spectra of DMSO, DMF and ethanol solutions of this complex were very similar they differed somewhat from that obtained in pyridine (Table II). In particular, the peak maxima in the latter spectrum appeared as shoul-ders on a rising absorption. These solution spectra were recorded in dry de-oxygenated solvent systems and were observed to be little changed over a period of several days.

The solid-state and solution spectra of Fe(acac)(dipic) are very similar, although the band at 20,200 cm^{-1} in the mull spectrum shifts to higher energy in solution. The spectra closely resemble the related data for Fe (acac)$_3$,[14] and are clearly consistent with a high-spin octahedral iron(III) complex in which the charge trans-

TABLE II. Spectral Properties for Complexes of Pyridine-2,6-Dicarboxylic Acid.

Complex		Electronic Absorption Maxima ($\times 10^{-3}$ cm^{-1})[a]	I.R. Spectra (Nujol Mull)
V(acac)(dipic)	N.M.[b] py DMSO[c]	23.8; 26.4; 32.9sh 16.4sh($\sim$35); 23.7; 28.5sh; 30.0sh 23.5(880); 26.6($\sim$1000)	1560vs[ν(C⸺O) of acac]; 1338vs, 1625vs and 1690vs[ν(COO) of dipic].
V(OH)(dipic)·2H$_2$O	N.M.	14.7; 26.3; 30.3sh	1385s and 1665vs[ν(COO) of dipic]; 3460s and $\sim$3200s, br [ν(OH)].
VO(dipic)·2H$_2$O	N.M.	13.3; 27.8sh; 30.2sh	985s[ν(V=O)]; 1355s and 1670vs[ν(COO) of dipic]; $\sim$3150s, vbr[ν(OH)].
VO(dipic)(bipy)	N.M.	13.5; 21.5sh; 24.0	968s[ν(V=O)]; 1333s and 1673vs[ν(COO) of dipic].
VO(dipic)(phen)·$^1/_2$H$_2$O	N.M.	13.5; $\sim$22.2sh; $\sim$26.3sh	968s[ν(V=O)]; 1332s and 1680vs[ν(COO) of dipic]; 3450w[ν(OH)].
Mn(acac)(dipic)·H$_2$O	N.M.	11.1; 13.2; 20.5sh; 20.9sh; 24.5sh	1525m–s, 1560mw and 1580mw[ν(C⸺O) of acac]; 1315s, 1630vs, 1660s and 1705vs [ν(COO) of dipic]; 3430m, br[ν(OH)].

TABLE II. (Cont.)

Complex		Electronic Absorption Maxima $(\times 10^{-3} \text{ cm}^{-1})^a$	I.R. Spectra (Nujol Mull)
Fe(acac)(dipic)	D.R.[d] N.M. EtOH[e]	~8.4?; 20.2 20.2; 28.6sh 22.45(1300); 28.6sh	1560s[ν(C≐O) of acac]; 1338s, 1608s and 1688s [ν(COO) of dipic].
Fe(acac)(dipic)·H$_2$O	D.R.	~8.5w,br?; 21.1	1570s[ν(C≐O) of acac]; 1365s, 1630s and 1658sh [ν(COO) of dipic]; 2450 m,br and 3500w[ν(OH)].
Co$_2$(dipic)(dipicH)$_2$·2H$_2$O	N.M.	~10.6[^{4}T$_{1g}$→^{4}T$_{2g}$]; 18.2sh, 18.9, 20.0 and 21.0sh[^{4}T$_{1g}$→^{4}T$_{1g}$(P)]	1380s, 1595s and 1625vs [ν(COO) of dipic]; 1725 sh[ν(COO) of dipicH or dipicH$_2$]; 3250m [ν(OH) of H$_2$O].
Co(dipic)(terpy)·3H$_2$O	N.M.	~10.9[^{4}T$_{1g}$→^{4}T$_{2g}$]; 15.9, 17.6 and 20.5sh[^{4}T$_{1g}$→^{4}T$_{1g}$(P)].	1380s, 1630vs, 1658s and 1675sh[ν(COO) of dipic]; 3380m, 3460m–s and 3540m–s[ν(OH) of H$_2$O].
Ni$_2$(dipic)(dipicH)$_2$	N.M.	9.8 and 10.9sh[^{3}A$_{2g}$→^{3}T$_{2g}$]; 15.4[^{3}A$_{2g}$→^{3}T$_{1g}$(F)]; 24.5sh[^{3}A$_{2g}$→^{3}T$_{1g}$(P)].	1380s, 1595s and 1625vs [ν(COO) of dipic]; 1730 sh[ν(COO) of dipicH or dipicH$_2$]; 3200sh and 3370 sh[ν(OH) of –COOH].
[Ni(dipic)]$_n$	N.M.	~9.3[^{3}A$_{2g}$→^{3}T$_{2g}$]; ~13.0[^{3}A$_{2g}$→^{3}T$_{1g}$(F)]; 24.0sh[^{3}A$_{2g}$→^{3}T$_{1g}$(P)].	1410s, 1582s, 1605vs and 1656s[ν(COO) of dipic].
Ni(dipic)(terpy)·3H$_2$O	N.M.	10.9sh and 12.5[^{f}[^{3}A$_{2g}$→^{3}T$_{2g}$]; 18.2[^{3}A$_{2g}$→^{3}T$_{1g}$(F)].	1380s, 1630vs, 1660s and 1675sh[ν(COO) of dipic]; 3370mw, 3460m and 3540ms[ν(OH) of H$_2$O].
Cu$_2$(dipic)(dipicH)$_2$	N.M.	7.6; 12.9	1380s, 1595vs and 1655s [ν(COO) of dipic]; 1715 m[ν(COO) of dipicH or dipicH$_2$]; ~2500m, br [ν(OH) of –COOH].
Cu$_2$(dipic)(dipicH)$_2$·EtOH	N.M.	7.6; 12.7	1340s, 1595s, 1660sh and 1675vs[ν(COO) of dipic]; 1710sh[ν(COO) of dipicH or dipicH$_2$]; ~2500m, br and ~3400 sh, br[ν(OH) of –COOH and EtOH].
Cu(dipic)(terpy)·3H$_2$O	N.M.	9.7; 14.9	1362s, 1625vs, 1655s and 1675sh[ν(COO) of dipic].

[a] For solution spectra ε_{max} values are given in parentheses. [b] N.M. = nujol mull. [c] Related spectra in DMF and EtOH very similar. [d] D.R. = diffuse reflectance. [e] Related spectra in py, DMSO and DMF very similar. [f] Closely spaced doublet.

fer band at ~20,000 cm^{-1} dominates the spectrum and largely obscures any of the very weak spin-forbidden d$\longleftrightarrow$d transitions of a $t_{2g}^3e_g^2$ system.

Although these spectra support the idea that there is no *gross* change in the metal environment upon going from the solid-state to solution, they do not clearly distinguish between a dimeric species and a monomer in which the solvent has been incorporated into the coordination sphere. The latter possibility is apparently the case since both V(acac)(dipic) and Fe(acac)(dipic) are monomers in ethanol,[17] and these complexes cannot be recovered unchanged from their solutions in polar solvents.

One unexpected result was the recovery of the hydrate Fe(acac)(dipic)·H$_2$O from solutions of Fe(acac)(dipic) in methanol or ethanol. Neither of these solvents was vigorously dried or the resulting solutions protected from the atmosphere so that the presence of a small amount of water can readily be accounted for. This complex has an electronic spectrum which resembles that of Fe(acac)(dipic) and an infrared spectrum characteristic of both coordinated dipic and acac (TableII). In addition to the expected ν(OH) water band at 3500 cm^{-1}, a broad feature of medium intensity is apparent at 2450 cm^{-1} which is characteristic of hydrogen bonding. This presumably arises through interaction between the water molecule and the carboxylate groups of the dipic ligand, and is a rather common feature in the solid state structures of hydrates of metal complexes of the pyridine carboxylic acids. Paralleling the occurrence of hydrogen-bonding, is an increase in the width of the highest energy ν(COO) band of dipic relative to that of the anhydrous complex.

When the vanadium complex was treated with water under controlled conditions, a bright yellow intermediate of stoichiometry [V(OH)(dipic)·2H$_2$O] was isolated before the final hydrolysis product VO(dipic)·4H$_2$O was formed. Its magnetic properties (Table I) and electronic absorption spectrum ($^3T_{1g}$(F)$\rightarrow$$^3T_{2g}$(F) transition at 14,700 cm^{-1}) are consistent with an octahedral

vanadium(III) species. The color of the complex and the absence of a ν(V=O) mode in its infrared spectrum rule out the presence of the vanadyl (VO^{2+}) moiety. Although it exhibits ν(COO) bands in the usual infrared spectral region at 1665 and 1385 cm^{-1} (Table II), additional sharp peaks at 1415(m)and 1535(m–s) cm^{-1}, which are not observed in the spectra of V(acac)(dipic) and VO(dipic)·4H$_2$O, may indicate that this complex contains some additional mode of carboxylate bonding. We have no direct evidence as to whether this is a hydroxy bridged dimer or not, since although the magnetic moment is lower than that expected for an S = 1 system, it is still within the range observed[18] for magnetically dilute vanadium(III) species.

The final product of the reaction between V(acac)(dipic) and water is the known complex VO(dipic)·4H$_2$O.[19] This readily reverts to the blue-grey dihydrate which is also the product of the reaction between VO(acac)$_2$ and pyridine-2,6-dicarboxylic acid in acetone. The nature of the latter complex was confirmed by its conversion to derivatives with 2,2'-bipyridyl and 1:10-phenanthroline, VO(dipic)(bipy) and VO(dipic)(phen)·^{1}/$_2$H$_2$O, respectively. All these complexes had infrared and electronic absorption spectra (Table II) characteristic of vanadyl VO^{2+} species and they are not considered further.

As an additional means of characterizing the vanadium complexes described in this work we recorded their X-ray photoelectron spectra. Vanadium 2p, carbon 1s and oxygen 1s electron binding energies for three of the vanadium complexes prepared in the present work, together with the related data for the reference compound VO(acac)$_2$, are presented in Table III. As has been our usual practice,[3, 8, 20, 21] these binding energies are quoted relative to a value of 284.0 eV for the carbon 1s binding energy of graphite. The binding energies were located with a precision of between ±0.1–0.2 eV and are generally considered accurate to ±0.2 eV relative to the above carbon 1s binding energy of graphite. Our data for VO(acac)$_2$ may be compared with the literature V 2p$_{3/2}$

TABLE III. X-Ray Photoelectron Spectra of Complexes of Pyridine-2,6-Dicarboxylic Acid.[a]

Complex	Metal		O 1s	C 1s	
	2p$_{1/2}$	2p$_{3/2}$			
VO(acac)$_2$	523.8	515.9	531.3	286.6	284.4
VO(dipic)·2H$_2$O	523.2	515.7	530.7	[b]	284.2
V(acac)(dipic)	~523.5	515.9	531.2	288.2	284.8
V(OH)(dipic)·2H$_2$O	523.4	515.4	531.2	288.2	285.0
Mn(acac)(dipic)	653.4	641.5	531.0	288.0	284.8
Fe(acac)(dipic)	–	–	531.0	288.2	284.8

[a] Binding energies are quoted relative to a value of 284.0 eV for the C 1s binding energy of graphite. [b] This higher energy C 1s peak was too weak and broad to be located with sufficient accuracy to justify its inclusion.

and O 1s binding energies for this complex reported by Larsson *et al.*,[22] as measured on a AEI ES100 instrument relative to a platinum $4f_{7/2}$ value for platinum foil of 71.0 eV. Our values (Table III) are 0.9 eV higher than these and this may be due to some degree of surface charging. Indeed, the C 1s values of coordinated acac in this complex are ~0.8 eV higher than those we previously observed[21] in the spectrum of Sc(acac)$_3$, a shift which is consistent with this interpretation.

A comparison of the V 2p binding energies in Table III reveals very little dependence upon the formal metal oxidation state, a conclusion which is in accord with the observations of Murray and Sheahan[23] who studied the V 2p binding energy spectra of several other complexes of vanadium(IV) and vanadium(III). However, two of the complexes in Table III, VO(dipic)·2H$_2$O and V(OH)(dipic)·2H$_2$O, contain rather similar metal environments with a single identical organic ligand molecule. The C 1s binding energy spectra of complexes of the pyridine carboxylic acids are characterized by two peaks,[8,21] the one at higher energy being due to the carboxylate carbon atoms and that at lower energy to the carbon atoms of the aromatic rings. Since we would not expect these carbon binding energies to be significantly different between the two complexes mentioned above, they provide a reasonable means of internally referencing the V 2p energies. When we reference V 2p to some constant C 1s binding energy, for example 284.2 eV for the more intense lower energy component, then the V $2p_{1/2,3/2}$ energies follow the sequence V(OH) (dipic)·2H$_2$O < VO(dipic)·2H$_2$O, which is consistent with our contention that V(OH)(dipic)·2H$_2$O is an authentic complex of vanadium(III).

In the reaction between Mn(acac)$_3$ and pyridine-2,6-dicarboxylic acid we were unable to isolate a pure complex of stoichiometry Mn(acac)(dipic). Although the product exhibited an infrared spectrum characteristic of coordinated dipic and acac, this spectrum is not identical with that of either the related vanadium or iron complex, and neither is this product isomorphous with these species. Also, the infrared spectrum revealed the presence of a relatively prominent ν(O–H) absorption close to 3400 cm^{-1}. Accordingly, this complex is formulated as "Mn(acac)(dipic)·H$_2$O" in Tables I–III. It is unstable when stored for any length of time at room temperature and it is most likely authentic Mn(acac) (dipic) always contaminated with some decomposition product. Its room temperature magnetic moment of 4.63 B.M. is consistent with this suggestion, and its electronic absorption spectrum (Table II) possesses band maxima which reveal a striking similarity with those shown in the related spectrum of magnetically dilute Mn(pic)$_3$·H$_2$O (picH = pyridine-2-carboxylic acid).[24]

The manganese 2p, oxygen 1s and carbon 1s binding energies of this complex are listed in Table III, together with some related data for Fe(acac)(dipic). The relative intensities of the two C 1s peaks in the spectrum of Mn (acac)(dipic)·H$_2$O are identical with the related peaks in the spectrum of Fe(acac)(dipic), a result which supports our formulation of this complex. The value of the energy difference δ(Mn2p$_{3/2}$,O1s), which has been considered as indicative of the manganese oxidation state in a series of complexes containing rather similar ligand arrangements,[24,25] is 110.5 eV. This is close to the value of 110.7 eV for Mn(acac)$_3$,[25] but unfortunately, a suitable manganese(II) derivative was not available to provide the corresponding δ(Mn2p$_{3/2}$,O1s) value for a manganese species one oxidation unit lower.

$M(acac)_2$

In contrast to the reactions of pyridine-2,6-dicarboxylic acid with aqueous solutions of cobalt(II), nickel (II) and copper(II) salts to form hydrated 1:1 and 1:2 complexes,[3,11,26,27] the corresponding acetylacetonates react in acetone to form the 2:3 complexes (Table I). The cobalt(II) complex was isolated as the dihydrate but other than a fairly intense ν(O–H) band due to water, its infrared spectrum was essentially identical to that of its nickel analogue. These spectra are in turn slightly different from the related spectrum of the copper complex (Table II), particularly in the ν(COO) region. All three complexes exhibited a high energy band at ~1720 cm^{-1}, assigned to ν(COO) of the dipicH or dipicH$_2$ moiety. In addition, ν(O–H) bands characteristic of the –COOH group were observed at ~3300 cm^{-1} in the spectrum of the nickel complex, but in the related copper complex these features had largely been replaced by a band at ~2500 cm^{-1} assigned to ν(O–H) of 'a hydrogen bonded –COOH group. These spectral differences are not surprising when it is remembered that in its other pyridine-2,6-dicarboxylate complexes, copper (II) has revealed a different structural chemistry from that of cobalt(II) and nickel(II), as for instance in the hydrated 1:2 complexes Cu(dipic)(dipicH$_2$)·3H$_2$O[7] and M(dipicH)$_2$·3H$_2$O, where M = Co or Ni.[3,26] Two possibilities are reasonable for the formulation of the 2:3 complexes, namely M$_2$(dipic)(dipicH)$_2$ or M$_2$ (dipic)$_2$(dipicH)$_2$, but a distinction between them is not feasible without a single crystal X-ray structure analysis. However, the infrared spectral differences we observed between the cobalt and nickel complexes and the copper derivative, particularly in the region above 1500 cm^{-1}, may arise because of the above structural differences. For convenience these complexes are all formulated as M$_2$(dipic)(dipicH)$_2$ in Tables I and II.

The 2:3 complexes react with 2,2′,2″-terpyridyl in an identical fashion to afford the mixed ligand derivatives M(dipic)(terpy)·3H$_2$O. On the other hand, they exhibit quite different behavior when refluxed in ethanol, the cobalt(II) and nickel(II) complexes being converted to polymeric [Co(dipic)]$_n$[3] and [Ni(dipic)]$_n$, while the copper(II) complex affords a product which we formulate as Cu$_2$(dipic)(dipicH)$_2$·EtOH. Polymeric

$[M(dipic)]_n$ have identical infrared spectra while the related spectrum of $Cu_2(dipic)(dipicH)_2 \cdot EtOH$ closely resembles that of $Cu_2(dipic)(dipicH)_2$ with some change in the $\nu(COO)$ region.

The electronic absorption spectra of the new cobalt (II) and nickel(II) complexes of pyridine-2,6-dicarboxylic acid (Table II) are very similar to those of other pyridine carboxylate complexes of these two metal ions which are known to possess pseudo-octahedral structures.[1,3,28,29] Accordingly, it seems most likely that within the complexes $M_2(dipic)(dipicH)_2$ and $[M(dipic)]_n$ distorted octahedral geometries prevail. The nujol mull electronic absorption spectra of the copper(II) complexes exhibit two absorption bands characteristic of highly distorted octahedral copper(II) species. The spectrum of $Cu(dipic)(terpy) \cdot 3H_2O$ closely resembles that of its related dihydrate,[10] while the corresponding transitions of $Cu_2(dipic)(dipicH)_2$ and its ethanolate are, as expected,[10] shifted to lower energy.

Acknowledgements

References

1 ˙Part VII. J. Michel and R.A. Walton, *J. Inorg. Nuclear Chem., 36*, 000 (1974).

2 Address any correspondence to this author.

3 R.W. Matthews, A.D. Hamer, D.L. Hoof, D.G. Tisley and R.A. Walton, *J. Chem. Soc., Dalton Trans.*, 1035 (1973).

4 D. Grendić and B. Korpar–Čolig, *Inorg. Chem., 3*, 1328 (1964).

5 M.M. Jones, *J. Am. Chem. Soc., 81*, 3188 (1959).

6 P.W.N.M. van Leeuwen and W.L. Groeneveld, *Inorg. Nucl. Chem. Lett., 3*, 145 (1967).

7 R.L. Dutta and S.Ghosh, *J. Ind. Chem. Soc., 44*, 296 (1967).

8 D.L. Hoof, D.G. Tisley and R.A. Walton, *J. Chem. Soc., Dalton Trans.*, 200 (1973).

9 K. Nakamoto, *"Infrared Spectra of Inorganic and Coordination Compounds"*, Wiley–Interscience, 1970, p. 247.

10 D.P. Murtha and R.A. Walton, *Inorg. Chim. Acta, 8*, 279 (1974).

11 See for example, M. Biagini Cingi, A. Chiesi Villa, C. Guastini and M. Nardelli, *Gazz. Chim. Ital., 101*, 825 (1971).

12 See for example, S. Koda, S. Ooi, H. Kuroya, Y. Nishikawa, Y. Nakamura and S. Kawaguki, *Inorg. Nucl. Chem. Lett., 8*, 89 (1972).

13 J.S. Wood, *Prog. Inorg. Chem., 16*, 311 (1972).

14 D.W. Barnum, *J. Inorg Nucl. Chem., 21*, 221 (1961).

15 A nujol mull spectrum of $V(acac)_3$ exhibits absorption maxima at $\sim 18,000(sh)$, $22,100(sh)$, $23,400(sh)$ and $25,000$ cm^{-1}.

16 A.B.P. Lever, *"Inorganic Electronic Spectroscopy"*, Elsevier, 1968, p. 268.

17 $V(acac)(dipic)$: Found 313, Calcd. 315; $Fe(acac)(dipic)$: Found 321, Calcd. 320.

18 H. Böhland and P. Malitzke, *Z. Anorg. Chem., 350*, 70 (1967).

19 G.H. Bersted, R.L. Belford and I.C. Paul, *Inorg. Chem., 8*, 1557 (1968).

20 D.G. Tisley and R.A. Walton, *J. Mol. Struct., 17*, 401 (1973).

21 A.D. Hamer, D.G. Tisley and R.A. Walton, *J. Inorg. Nucl. Chem., 36*, 1771 (1974).

22 R. Larsson, B. Folkesson and G. Schön, *Chemica Scripta, 3*, 88 (1973).

23 K.S. Murray and R.M. Sheahan, *J. Chem. Soc., Dalton Trans.*, 1182 (1973).

24 D.L. Hoof, D.G. Tisley and R.A. Walton, *Inorg. Nucl. Chem. Lett., 9*, 571 (1973).

25 J. Sheets, D.G. Tisley and R.A. Walton, *J. Inorg. Nucl. Chem., 35*, 3541 (1973).

26 H. Gaw, W.R. Robinson and R.A. Walton, *Inorg. Nucl. Chem. Lett., 7*, 695 (1971).

27 M. Biagini Cingi, A. Chiesi Villa, C. Guastini and M. Nardelli, *Gazz. Chim. Ital., 102*, 1026 (1972).

28 A. Anagnostopoulos, R.W. Matthews and R.A. Walton, *Canad. J. Chem., 50*, 1307 (1972).

29 R.W. Matthews and R.A. Walton, *Inorg. Chem., 10*, 1433 (1971).