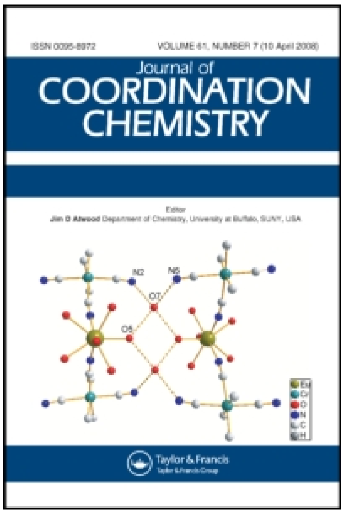

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SOME METAL(II) COMPLEXES OF POTENTIALLY TERDENTATE HETEROCYCLIC SCHIFF BASES

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Complexes of copper(II), cobalt(II) and oxovanadium(IV) with Schiff bases obtained by condensing salicylaldehyde, substituted salicylaldehydes and 2-hydroxy-1-naphthaldehyde with 2-aminopyridine (ampy), 5-methyl-2-aminopyridine (CH_3ampy) and 4-aminopyridine (4-ampy) have been synthesized and characterized. Two types of complexes [$MLCl(H_2O)_n$ and ML_2] were obtained, depending on whether the metal chloride or metal acetate was used for the synthesis. There is evidence that the three donor atoms are involved in bonding, with the phenoxide O and one of the N atoms bonding strongly to the same metal while the other N atom is involved in bridging.

Keywords: Schiff base, first row, complexes, synthesis

INTRODUCTION

The ligands *N*-salicylidene-2-iminopyridines (I) (and *N*-naphthylidene-2-iminopyridines) and their 4-aminopyridine analogues are potentially terdentate. Although it seems[1–3] that the ligands (I) are bidentate, bonding *via* the phenoxide O and an N atom, it is not clear which of the two N atoms preferentially coordinates to the metal. Earlier reports[1–3] favour the azomethine N atom in contradiction of an obvious preference for the hetero N atom which is more basic.[3–6] Studies[7,8] embarked upon recently in our laboratory have established the relevance of steric and electronic factors, ring-size and the metal ion in determining which of the N atoms preferentially bonds to the metal.

In studies involving zinc, cadmium, and mercury,[8] (I) appeared to be bidentate, bonding to the metals through the hetero N and the phenoxide O atoms. On the other hand, in the naphthyl analogue, the three donor atoms participate in bonding. We also observed that the ligands preferentially bond to palladium(II) and platinum(II) through O and endocyclic N atoms.[9] Encouraged by these results, we have re-investigated the copper(II) and cobalt(II) complexes of (I) and have extended the work to the naphthylidene analogues. We have included two complexes where the hetero N atom is furnished by 4-aminopyridine (*i.e.*, the azomethine N is *para* to the hetero N atom).

EXPERIMENTAL

Preparation of the complexes

Copper and cobalt complexes were prepared by reacting methanolic solution of the metal acetate with a methanolic solution of the preformed ligands in a mole ratio of

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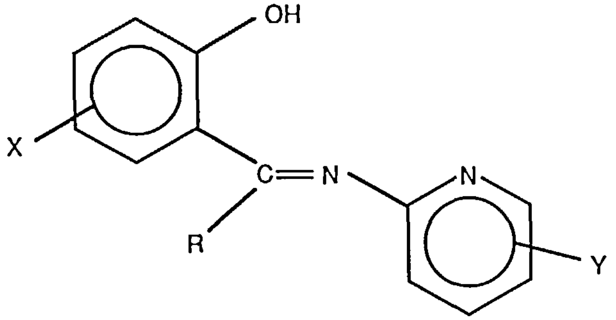

R	X	Y	Ligand
H	H	H	H-sal-ampy
H	H	5-CH_3	H-sal-CH_3ampy
H	3-OCH_3	H	H-Omesal-ampy
H	5-NO_2	H	H-NO_2sal-ampy
CH_3	H	H	H-7-CH_3sal-ampy

I

1:2.[1] However, efforts made to obtain Cu(Omesal-ampy)$_2$ from copper(II) acetate gave a viscous liquid from which we could not isolate any solid product. This complex was obtained by reacting a methanolic solution of $CuCl_2.2H_2O$ with H-Omesal-ampy and buffering with Et_3N. Cu(CH_3sal-ampy)$_2$ was obtained by templating 2-hydroxyacetophenone, 2-aminopyridine and copper(II) acetate (2:2:1 mole ratio). Cu(sal-4-ampy)$_2$,4H_2O was prepared by templating the appropriate aldehyde with 4-aminopyridine in the presence of $CuCl_2.2H_2O$ and buffering the medium with Et_3N. The oxovanadium(IV) complexes were prepared either by reacting a methanolic solution of $VOSO_4$ with a methanolic solution of the preformed ligands [for VO(sal-CH_3ampy)$_2$ and VO(naph-CH_3ampy)$_2$] or by reacting a methanolic solution of syrupy $VOCl_2$ with a hot methanolic solution of the aldehyde and the amine (for [VO(sal-4-ampy)Cl.$\frac{1}{2}H_2O$] and [VO(naph-4-ampy)Cl]). All the complexes were isolated as powders and after thorough washing with methanol, dried over conc. H_2SO_4 *in vacuo.*

Physical measurements

Microanalysis was carried out by the microanalytical laboratories of the University of Ibadan and of the University College, Dublin. The i.r. spectra were run on Perkin Elmer FTIR 1700 (4000–400 cm^{-1}) and Perkin Elmer 283 grating spectrometers (4000–200 cm^{-1}) using pressed KBr discs. The electronic spectra (900–190 nm) in solid and solution ($CHCl_3$ and pyridine) were run on a Perkin Elmer 552 spectrophotometer. The diffuse reflectance spectra of the copper(II) complexes were

Compound	ν(C=N)	ν(C–O)	Pyridine ring vibrations				ν(V=O)	M–Cl
			8a	–	6a	16b		
Cul(sal-anil)$_2$	1588vs	1330s						
	(1620)	(1285)						
Cu(sal-ampy)$_2$	1610vs	1328s	1590s					
	(1612)	(1283)	(1591)		(623)	(406)		
[Cu(Omesal-ampy)Cl.H$_2$O]^e	1611br	1340s		1248w				380^c
	(1608)	(1258)	(1592)		(622)	(408)		
Cu(Clsal-ampy)$_2$	1610vs	1322s	1590s	1246w	660m	414w		
	(1612)	(1284)	(1592)					
Cu(Brsal-ampy)$_2$	1609vs	1302s	1590m	1222w	643w	440w		
	(1612)	(1284)	(1590)					
Cu(NO$_2$sal-ampy)$_2$	1610br	1320s	1598s	1246w	652m	440w		
	(1616)	(1301)	(1594)		(592)	(408)		
Cu(CH$_3$sal-ampy)$_2$	1606vs	1340s	1588s	1254w				
Cu(sal-4-ampy)$_2$.4H$_2$O^e	1615vs	1332s	1526s		661m			
Cu(naph-ampy)$_2$	1617vs	1368s	1603s	1252	660w	417w		
	(1620)	(1290)	(1592)	(1248)	(594)	(405)		
Cu(naph-CH$_3$ampy)$_2$	1618vs	1365s	1600s	1259m	656w	402m		
		(1289)	(1597)	(1250)	(649)	(412)		
Co(sal-ampy)$_2$	1607vs	1335s	1584m	1248w	630wm	411m		
Co(Omesal-ampy)$_2$	1606s	1332s	1586s		636wm	409w		
Co(NO$_2$sal-ampy)$_2$	1603vs	1316s	1587sh	1246w	653w	413w		
Co(naph-ampy)$_2$	1620vs	1300s	1615s	1249w	638w	415m		
VO(sal-CH$_3$ampy)$_2$	1606vs	1328s	1584vs	1251w	660w	408m	938vs	
[VO(sal-4-ampy)Cl.$\frac{1}{2}$H$_2$O]^e	1615sh 1597m	1362vs	1651vs		658w	427m	921 907 } vs	363m^c 331n^d
VO(naph-CH$_3$ampy)$_2$	1619vs	1398s	1600s 1600s	1252w 1256m	657w 656w	411w 409w	983 907 } vs	
[VO(napy-4-ampy)Cl.H$_2$O]^e	1618vs	1382	1600s	1256m	656w	409w	998 983 } vs	361w^c

[a] The corresponding ligand frequencies are given in parentheses for copper complexes only.

[b] The resolution of the spectra for copper complexes below 600 cm^{-1} is poor.

[c] M–Cl (terminal). [d] M–Cl–M (bridged). [e] A broad band at 3400–3300 cm^{-1} is assigned to ν(OH) from water; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

recorded using an SP500 spectrophotometer. Molar conductivities were measured on an MC-1 Mark V conductivity set.

RESULTS AND DISCUSSION

All the complexes (Table I), are either insoluble or only sparingly soluble in common organic solvents and therefore could not be recrystallised. They however analyse pure as ML_2 or [MLCl.nH_2O]. The complexes are non-electrolytes in DMF except [Cu(Omesal-ampy)ClH_2O] which behaves as a 1:1 electrolyte, thus suggesting some ligand exchange reaction.

Infrared spectra

The i.r. data are presented in Table I. The v(C=N) frequencies in the heterocyclic ligands occur at lower wavenumbers (1608–1612 cm^{-1}) than in Hsal-anil (1620 cm^{-1}) except in the naphthylidene analogues where v(C=N) (1620–1621 cm^{-1}) is comparable with Hsal-anil. Consequently the azomethine electrons in the Schiff bases involving 2-aminopyridines are more delocalised thus resulting in a more planar molecule than salicylideneiminobenzene. This also reduces the electron density on the azomethine N atom. While the v(C=N) mode suffers a substantial shift to lower wavenumbers (32 cm^{-1}) in Hsal-anil on chelation to copper, the shifts observed in Cu(II), Co(II) and VO(II) complexes of the pyridine analogues are much smaller (0–6, 5–13 and 3 cm^{-1}, respectively). The azomethine N atom is therefore only weakly involved in bonding in most of the complexes.

The pyridine sensitive modes, 8a and/or 6a and 16b are diagnostic of metal–pyridine interaction.[7,10–12] A positive shift upon complexation of these pyridine sensitive modes and/or the appearance of a weak band at 1240–1255 cm^{-1}, which is absent in most of the ligands, are strong indications[11] that the hetero N atom is involved in bonding to the metal ions. 8a shifts to lower wavenumbers in all the cobalt(II) complexes and remains virtually unchanged (± 2 cm^{-1}) in Cu(sal-ampy)$_2$, Cu(Clsal-ampy)$_2$ and Cu(Brsal-ampy)$_2$. In all the other complexes 8a shifts to higher wavenumbers. However, the involvement of the hetero N atom in bonding in [Cu(Omesal-ampy)Cl.H_2O], Cu(NO_2sal-ampy)$_2$, Cu(CH_3sal-ampy)$_2$, Cu(naph-ampy)$_2$, Cu(naph-CH_3ampy)$_2$ and the oxovanadium(IV) complexes is supported by the appearance of a weak band at 1248, 1246, 1254, 1260 and 1259 cm^{-1}, respectively.

In all the complexes v(C–O) frequencies shift to higher wavenumbers indicating that the phenoxide O atom is involved in bonding.[13] Consequently, these ligands are more prone to coordinating *via* the phenoxide O and the endocyclic N atoms leaving the azomethine N atom free to participate in intermolecular N---M---N linkages. In the Schiff base complexes involving 4-aminopyridine, the hetero N atom is expected to participate in any such intermolecular bonding.

The v(V=O) frequencies (938–1000 cm^{-1}) are normal[14] for 5-coordinate VO^{2+} complexes in VO(sal-CH_3ampy)$_2$ and VO(naph-CH_3ampy)$_2$. The appearance of a second very strong band at 907 cm^{-1} in VO(naph-CH_3ampy)$_2$ coupled with the split of the v(V=O) bands in VO(sal-CH_3ampy)$_2$, and a substantial reduction of this frequency in VO(sal-CH_3ampy)$_2$ (938 cm^{-1}) would suggest that these oxovanadium(IV) complexes are not simple monomers and indeed the VO group may exist in more than one environment. One of the oxovanadium(IV) complexes, [VO(sal-4-ampy)Cl.$\frac{1}{2}H_2O$], is yellow. Its v(V=O) frequencies of 921 and 907 cm^{-1} (split) indicate that although there may not be any V=O—V=O linkages, the complex is six-coordiante and not monomeric.

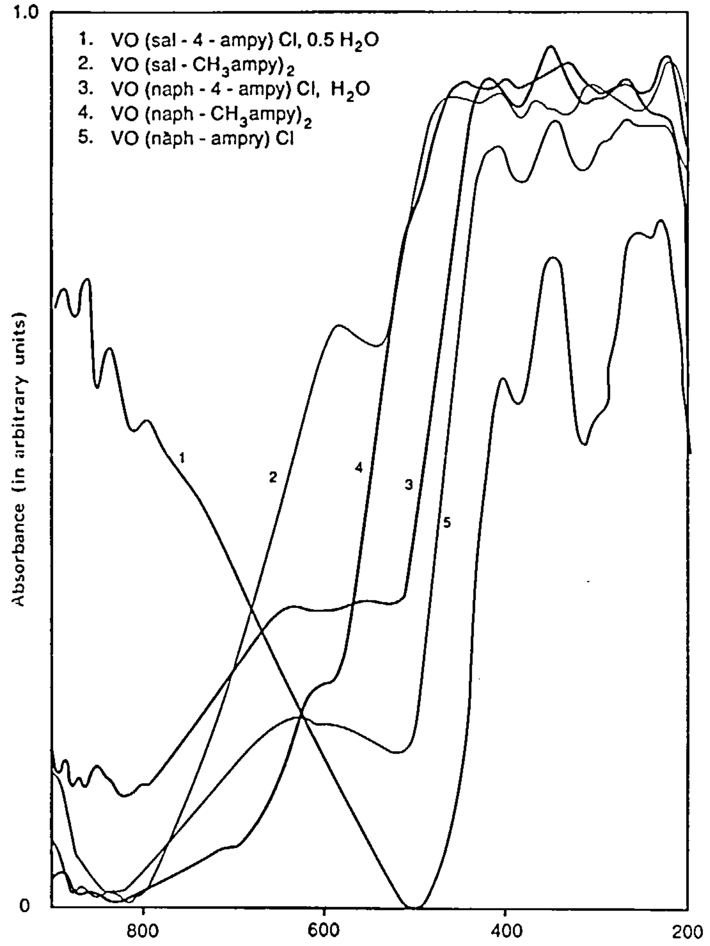

FIGURE 1 Reflectance spectra of the VO(II) complexes.

Electronic spectra

The spectra of the copper(II) complexes are characterised by a low-intensity, asymmetric and broad band between 13–17 kK, tailing into the near i.r. region. In most cases, the band is split. The corresponding bis-salicylaldiimineaniline complex shows a more intense and less broad band in the same region. Consequently, it can be concluded that the presence of the hetero N atom exerts some definite stereochemical influence on the copper complexes. The spectral properties of the copper complexes conform with those expected for tetragonally elongated, distorted, octahedral geometry. The three transitions predicted[15] are observed at 10.3–11.8 kK $({}^2A_{1g} \leftarrow {}^1B_{1g})$, 13.6–14.3 kK $({}^2E_g \leftarrow {}^2B_{1g})$ and 17–18.2 kK $({}^2B_{2g} \leftarrow {}^2B_{1g})$ for Cu(Clsal-ampy)$_2$,

$Cu(NO_2sal\text{-}ampy)_2$ and $Cu(naph\text{-}ampy)_2$. In the other copper complexes the low energy transition appears to be below 10.5 kK except in the cases of $Cu(sal\text{-}anil)_2$ and $[Cu(Omesal\text{-}ampy)Cl.H_2O]$, which are obviously pseudotetrahedral.

Similarly, the spectra of the cobalt(II) complexes are typical of octahedral complexes. The three bands predicted[16,17] for octahedral cobalt(II) complexes are observed, except in $Co(NO_2sal\text{-}ampy)_2$ where v_2 is not observed. The observed bands are thus assigned as follows: v_1: ${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$, 11–12.5 kK; v_2(shoulder): ${}^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$, 14–15 kK; v_3: ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$, 16–20 kK. This is consistent with the red colour[17] of the cobalt complexes.

The electronic spectra of the oxovanadium(IV) complexes (Figure 1) reflect a diversity of geometries. Most of them gave three or four bands with the exception of $[VO(sal\text{-}4\text{-}ampy)Cl.\frac{1}{2}H_2O]$ which have two bands, where no band was observed at 14–18 kK. Consequently, $[VO(sal\text{-}4\text{-}ampy)Cl.\frac{1}{2}H_2O]$ is six-coordinate[18] while the others are five-coordinate with stereochemistry varying between C_{2v} (four bands) and C_{4v} (three bands).[19] The following assignments, based on the energy level sequence[19] $b_2(d_{xy}) < b_1^*(d_{x^2-y^2}) < e_\pi^*(d_{xz},d_{yz}) < a_1^*(d_{z^2})$ are made: $b_1^* \leftarrow b_2$(11–12 kK), $e_\pi^* \leftarrow b_2$ (split in C_{2v} symmetry) 14–17.5 kK, and $a_1^* \leftarrow b_2$ (19.5–22 kK). The bands at 21–29 kK in copper(II), cobalt(II) and oxovanadium(IV) complexes are due to charge-transfer transitions.

The room temperature magnetic moments for the copper(II) complexes are normal (1.8–2.0 BM) for a d^9 system. The moments for the cobalt complexes (4.4–4.7 BM) confirm three unpaired electrons but seem slightly low for octahedral cobalt(II) complexes; those for the oxovanadium(IV) complexes (1.7–1.8 BM) are normal for a d^1 configuration, thus excluding the possibility of any direct metal-metal interaction.

It can be concluded from this study that the three donor atoms in the ligand (I) are involved in bonding in the copper and cobalt complexes except that whereas the phenoxide O and one of the N atoms bond to the same metal atom, the third donor atom is involved in bridge formation, leading to distorted octahedral geometry. A diversity of geometries is observed for the oxovanadium(IV) complexes (which are not simple monomers), but no evidence for direct metal–metal interaction is to hand.

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