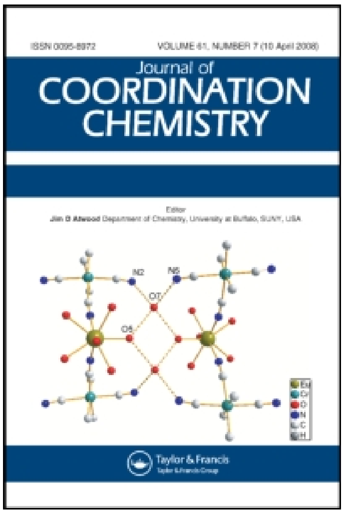

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BIS[(4-AMINO-2-METHYL-5-PYRIMIDINYL-METHYLTHIO)ACETATO] COBALT(II), NICKEL(II) AND COPPER(II) COMPLEXES

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Cobalt(II) nickel(II) and copper(II) complexes of (4-amino-2-methyl-5-pyrimidinyl methylthio) acetate have been synthesized and characterised. All the complexes are paramagnetic with coordination involving a sulphur atom and the oxygen atom of the carboxylate group. Cobalt(II) is four-coordinate, nickel(II) is six-coordinate while copper(II) is five-coordinate. Although the complexes are non-electrolytes in DMF and DMSO, they are found to be amphoteric.

Keywords: complexes, nickel, cobalt, copper, synthesis, thiamine analogues

INTRODUCTION

Recently,[1] we reported platinum(II) and palladium(II) complexes of (4-amino-2-methyl-5-pyrimidinylmethylthio)acetate (AMMPTA) which are, perhaps, the first examples of complexes of thiamine derivatives where sites alternative to the N(1') position of the pyrimidine ring are coordinated. We have found this ligand to be unique in that it contains a wide variety of coordination sites in addition to be being amphoteric (Figure 1). Secondly, the comparison of the donor properties of this ligand is more straightforward than in the parent thiamine molecule where the pyrimidine ring is conjugated with the thiazolium ring.[2-6] Our main objective is to create an environment whereby the ligand could act as a bidentate. It is our belief that in basic

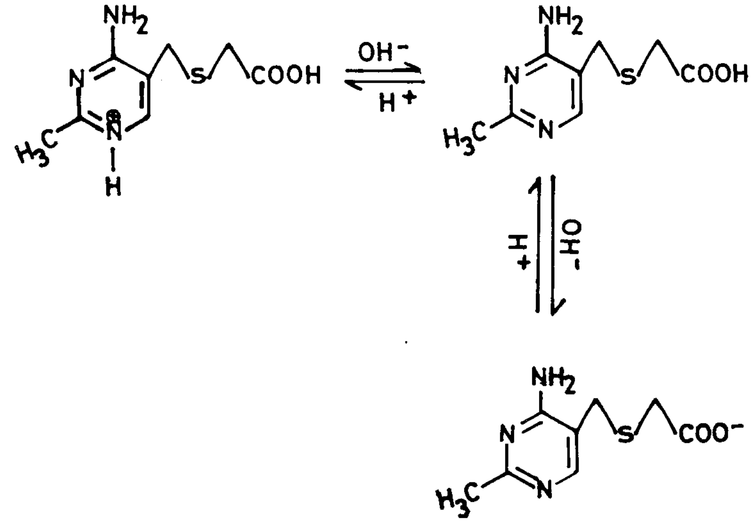

FIGURE 1 Acid-base behaviour of AMMPTA.

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TABLE I
Analytical data for the Co(II), Ni(II) and Cu(II) complexes.

Compound	Colour	M.P.(°)	Yield(%)	Analysis, Found (Calcd.) % C	H	N	metal	μ_{eff} (B.M.)
(1) AMMPTA	White	288-290	70	44.98 (45.04)	5.09 (5.16)	19.69 (19.72)		
(2) Co(AMMPTA)$_2$	Pink	208-210	68	39.81 (39.75)	4.11 (4.14)	17.28 (17.39)	12.09 (12.18)	4.48
(3) Ni(AMMPTA)$_2$·2H$_2$O	Green	220-220[a]	65	37.12 (37.02)	4.59 (4.63)	16.08 (16.17)	11.38 (11.31)	2.93
(4) Cu(AMMPTA)$_2$· H$_2$O	Violet	212-214	72	37.14 (37.08)	4.39 (4.35)	16.58 (16.62)	12.62 (12.56)	1.86

[a] Decomposes.

medium where the carboxylic acid group is fully ionized, the ability of this ligand to act as a bidentate would be enhanced.

In continuing our investigation on potential bidentate ligands which are based on thiamine, we report the syntheses and characterization of bis[(4-amino-2-methyl-5-pyrimidinylmethylthio)acetato cobalt(II), nickel(II) and copper(II) complexes.

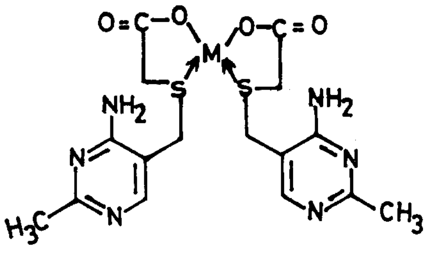
EXPERIMENTAL

The ligand, AMMPTA, was synthesized according to a literature method.[7] Cobalt(II), nickel(II) and copper(II) complexes were prepared as described earlier[1,8] except that acetate metal salts were used in this work. The i.r. spectra were taken in KBr discs using a Perkin Elmer 457 spectrometer in the range 4000–250 cm^{-1}. The reflectance spectra were run on a Unicam SP500 spectrophotometer equipped with a reflectance attachment using A.R. $CaCO_3$ as the reference. The room temperature magnetic moments were determined using the Gouy method and employing $Hg[Co(SCN)_4]$ as the calibrant. The conductivity measurements were carried out in DMSO and DMF with an Electrolytic Conductivity Model MC-1, Mark V, while the nmr spectra were run in DMSO-d_6 on a Varian T-60A nmr spectrometer. Analytical data are given in Table I.

RESULTS AND DISCUSSION

Like the ligand itself, all the three complexes are soluble in both acid and alkali showing that they are amphoteric. The complexes are generally insoluble in most organic solvents. Cobalt(II) and copper(II) complexes are readily soluble in DMSO and DMF whereas the nickel(II) complex dissolved in these solvents only on heating. The ready solubility of both the cobalt(II) and copper(II) complexes in DMF and DMSO, both of which are coordinating solvents, suggests axial ligation. For the nickel(II) complex where water molecules are believed to occupy the fifth and sixth positions of the coordination sphere, solubility is rather poor, showing that the water molecules are strongly bonded. *Cis* and *trans* structures (I(a) and (b)) have been proposed for these complexes. The poor conductivity behaviour (<10 ohm^{-1} cm^2 mol^{-1}) of the solutions of the complexes in DMSO and DMF confirms that they are non-electrolytes in these solvents. The low conductivities observed may be due to traces of impurities.

I (a)



I (b)

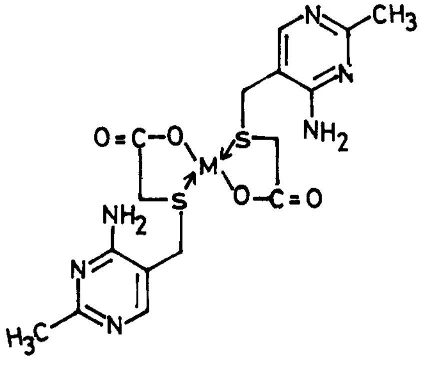


Table II lists tentative i.r. assignments for the complexes. Evidence for the participation of the carboxylate group in coordination is reflected in the shift of the C = 0 stretching frequencies in the ligand from 1650 cm^{-1} to 1660 cm^{-1} in the cobalt(II) and nickel(II) complexes, and to 1640 cm^{-1} in copper(II) complex. The bands at 3300 and 3160 cm^{-1} in the ligand are due to NH_2 (asym and sym) stretching frequencies which remain unchanged in the three complexes. This finding is consistent with the assumption that the metal ions are not coordinated to the NH_2 group of the ligand. The band at 1580 cm^{-1} in the ligand is assigned to the ν(C=N) mode which remains unchanged in the complexes, suggesting non-involvement of the pyrimidine ring in coordination. This observation is contrary to our experience with other thiamine complexes reported earlier.[4,9] The band at 1370 cm^{-1} in the ligand is ascribed to the ν(C-N) frequency which remains the same in the complexes. Although the N(1′) position of the ligand is open to attack under our experimental conditions, it seems that chelate effect involving the two donor atoms (S and O) in close proximity is important. The non-involvement of the NH_2 group in bonding is possibly due to the participation of the lone pair of electrons on the nitrogen atom of the NH_2 group in the pi system of the pyrimidine ring. Its positive charge would be unfavourable for complexation. The new bands at 1220, 795 and 690 cm^{-1} in the cobalt(II) complex, 1225, 790 and 600 cm^{-1} in the nickel(II) complex, and 1240, 790 and 600 cm^{-1} in the copper(II) complex are assigned to ν(M-S).[10] It is to be noted that these bands are not present in the ligand. Other bands of interest are at 415 cm^{-1} in the cobalt(II) complex, 410 and 380 cm^{-1} in the nickel(II) complex and 440 and 400 cm^{-1} in the copper(II) complex which are ascribed to the ν(M-O) mode. The band between 3500 and 3400 cm^{-1} in the nickel(II) and copper(II) complexes is assigned to ν(HOH) since this band is absent in the ligand as well as in the cobalt(II) complex. This observation is in support of our assumption that water is coordinated to the copper(II) and nickel(II) ions in their complexes.

TABLE II
Relevant infrared frequencies (cm^{-1}) for the Co(II), Ni(II) and Cu(II) complexes.[a]

Co(AMMPTA)$_2$	Ni(AMMPTA)$_2$·2H$_2$O	CU(AMMPTA)$_2$· H$_2$O	Assignment
	3400-3500w	3400-3500w	ν(HOH)
3320w	3300w	3300w	
3100sh	3160br	3150w	ν(NH$_2$)
1660s	1660s	1650s	ν(C=0)
		1615s	
1580s, br	1580br	1580s	ν(C=N)
1370s	1370s	1370s	ν(C-N)
1280w	1280w	1270m	
1220m	1225m	1240s	
1200sh	1200sh	1200s	
795s	790m	790s	ν(M-S)
720sh	720w	710s	
690w	600w	600w	
590m, br	575br	440w	
415w	490w		ν(M-O)
	410w	400w	
	380w		

[a] S = strong, m = medium, br = broad, w = weak

Diffuse reflectance spectral data are tabulated in Table III. The cobalt complex is four-coordinate and therefore should have pseudo-tetrahedral geometry. For high-spin tetrahedral cobalt(II) complexes three spin-allowed electronic transitions from the quartet ground state to the excited states are expected.[11,12] The band between 17-20kK is assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ transition. The cluster of three bands in this region may be due to transitions to doublet excited states which acquire some intensity through spin-orbit coupling. A low-intensity band around 10kK is assigned to the $^4A_2 \rightarrow {}^4T_1(F)$ transition. The weak band at 24.7kK is likely to be charge-transfer in origin. The electronic spectrum of the nickel complex is consistent with octahedral geometry, and in agreement with i.r. and magnetic susceptibility data. The band at 10.7kK is assigned to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition while the band at 14-15kK is assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$. The shoulders near the band at 14kK may arise from spin-orbit coupling which mixes the $^3T_{1g}(F)$ and ^1Eg states.[13] The origin of the weak band at 19.4kK is unknown as the transition $^3T_{2g} \rightarrow {}^3T_{1g}(P)$ is expected at 25-30kK.[13,14] The spectrum of the copper complex shows an intense absorption at 17.9kK with two shoulders on the low frequency side. A similar spectrum has been reported[15] for pentaammine copper(II). In a tetrahedral environment absorption bands are expected at lower energy than 17kK.[16] Consequently this complex is most likely to have a square-

TABLE III
Diffuse electronic reflectance spectral data[a] for the complexes

Co(AMMPTA)$_2$	Ni(AMMPTA)$_2$·2H$_2$O	Cu(AMMPTA)$_2$· H$_2$O
10256	10695	10526
17240	12900sh	14184
18519	14085sh	15385sh
19608	15152	17094sh
24690		17857

[a] Band maxima in cm^{-1}. sh = shoulder.

pyramidal geometry, with a water molecule occupying the fifth position of the coordination sphere. The sequence for a square-pyrimidal stereochemistry (C_{4v}) is suggested[15] to be $^2G_1 < {}^2A_1 < {}^2B_2 < {}^2Eg$ with three transitions predicted. In this complex the transitions are 17.86kK ($^2B_1 \rightarrow {}^2Eg$), 14.18kK ($^2B_1 \rightarrow {}^2B_2$) and 10.53kK ($^2B_1 \rightarrow {}^2A_1$). The assignment is further strengthened by the observation[17] that the *trans*-ligand configuration of copper complexes in pyridine also shows enhanced absorption in the region 17–18kK.

If only states derived from $3d^7$ are considered, an assumption probably valid for most cobalt(II) complexes, all tetrahedral cobalt(II) complexes must be spin-free. Because the $^4A_2$ state is orbitally non-degenerate, an ion in this state should, to a first approximation, have the magnetic properties of an S state ion,[14] and, in particular, have a 'spin-only' value for its magnetic moment. However, our own observation for $Co(AMMPTA)_2$ along with data[14] for a number of other tetrahedral cobalt(II) complexes shows that in all cases tetrahedrally coordinated cobalt(II) does possess an orbital contribution to its magnetic moment. According to Holm and Cotton[15] this orbital contribution may be anywhere in the range of 0.2–1.1 B.M.,[18] depending on the nature of the ligands. A moment of 4.48 B.M. observed for $Co(AMMPTA)_2$ falls within this range. For $Ni(AMMPTA)_2{\cdot}2H_2O$ a moment of 2.93 B.M. observed is close to the 'spin only' value and falls within the range reported for octahedral nickel(II) complexes. A moment of 1.86 B.M. obtained for $Cu(AMMPTA)_2$ is normal for copper(II).

The broadness in the NMR spectra of all these complexes confirms their paramagnetic nature. In particular, it lends further support to the conclusion that $Ni(AMMPTA)_2$ is not a square planar complex.

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