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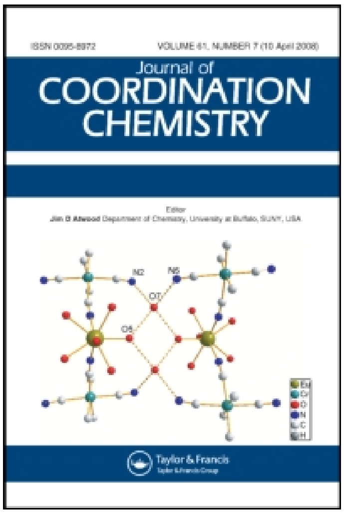

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Synthesis and Spectral Studies of Metal Complexes of 4-Xylosylamino-5-Nitroso-6-Oxopyrimidine Derivatives

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SYNTHESIS AND SPECTRAL STUDIES OF METAL COMPLEXES OF 4-XYLOSYLAMINO-5-NITROSO-6-OXOPYRIMIDINE DERIVATIVES

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(*Received 14 October 1991*)

Metal complexes of 1,6-dihydro-2-methylthio-5-nitroso-6-oxo-4-xylosylaminopyrimidine (A) and 1,6-dihydro-1-methyl-2-methylthio-5-nitroso-6-oxo-4-xylosylaminopyrimidine (B), were prepared and characterized by IR, electronic, ^{1}H and ^{13}C-NMR spectroscopies and magnetic and thermal measurements. In all the isolated complexes the organic ligands act as chelating agents through the O atom substituted at C6 and the NO group substituted at C5 of the pyrimidine rings, except in one of the Ag(I) complexes, where coordination takes place *via* the S atom of the SCH_3 group substituted at C2 of the pyrimidine ring.

Keywords: Metal complexes, pyrimidine derivatives, NMR studies

INTRODUCTION

Interest in the study of metal complexes of heterocyclic compounds containing sulphur stems from the biological activity of many of them.[1–4] Within these compounds, thiopyrimidine derivatives are highlighted because of their wide range of biological activity (*e.g.*, some of them can act as inhibitors and antimetabolites)[5], whereas 2-thiopyrimidine shows strong *in vitro* bacteriostatic activity towards *E. coli* and 6-amino-2-thiouracil is well known because of its antiviral,[6] and 6-amino-2-thiouracil because of its antiviral and chemitherapeutic activities.[7] In many of these cases it seems probable that the formation of metal complexes results in their biological action.[8–10]

In this paper we present results concerning the synthesis and study of metal complexes of the pyrimidine nucleoside analogue 1,6-dihydro-1-methyl-2-methylthio-5-nitroso-6-oxo-4-xylosylaminopyrimidine (B). A previous study on this compound[11] pointed out that its coordination to Au(III) and Pd(II) ions takes place through the O atom and NO group, substituted at C6 and C5 of the pyrimidine ring, respectively. With the aim of studying the ability of coordination of N1 in competition with C5–NO groups, we have also carried out reactions between some metal ions and the compound 1,6-dihydro-2-methylthio-5-nitroso-6-oxo-4-xylosylaminopyrimidine (A).

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EXPERIMENTAL

Preparation of the ligands and complexes

The two organic pyrimidine nucleoside analogues were prepared by a method previously reported by one of the authors.[12]

Ni(II)/A, Ni(II)/B and Cu(II)/A complexes were synthesized by stirring a mixture formed by suspension of the organic ligand (2 mmol) in dioxane and a saturated aqueous solution of the corresponding metal nitrate, in a molar ratio, ligand/metal, equal to 1/2, during one day at room temperature. The resulting solids were dissolved in ethanol and then precipitated by adding diethyl ether.

The remaining complexes were obtained by conventional precipitation at the pH values of the resulting solutions obtained by adding, under stirring, the corresponding metal nitrate to a hot solution (0.2 mmol) of the ligand in such a manner that the ligand/metal ratio was 2/1 in all cases; Co(II)/A, Ag(I)/A and Ag(I)/B complexes precipitated almost immediately. On the contrary, the Cu(II)/B system yielded a syrup which was diluted with ethanol and then the solid precipitated by adding diethyl ether.

All products were filtered by suction, dried in air and stored over P_4O_{10}.

Apparatus and methods

The acidic character of the two organic ligands, A and B, was determined by applying the Bjerrum method,[13] at variable ionic strengths and temperatures. For this, 25 cm^3 of a 10^{-3} M aqueous solution of the compound (A or B) were titrated against standardised 0.01 M NaOH solutions after adjusting the ionic strength (KCl). A Radiometer TTT60 titrator, fitted with glass and calomel electrodes, was used for recording pH.

Microanalyses (C, H and N) were performed in the Instituto de Química Bioorgánica (CSIC, Barcelona) and in the Servicios Tecnicos de la Universidad de Granada (STUGRA, Granada). Quantitative determination of metals in complexes were obtained from TG residues, which had been previously analyzed by IR spectroscopy. IR spectra were obtained with a Perkin Elmer 983G spectrophotometer in KBr (4000-250 cm^{-1}) and polyethylene (600–180 cm^{-1}) pellets. The ^1H and ^{13}C NMR spectra were recorded using a Bruker AM-300 spectrometer, in DMSO as solvent, with TMS as internal standard. Electronic spectra of the solid complexes were obtained with a Shimatzu MPC-3100 spectrophotometer in the 240–1500 nm range, and the magnetic measurements, at room temperature (20°C), of both ligands and complexes, with Faraday Bruker Magnet B-E15 equipment.

RESULTS AND DISCUSSION

Schematic representations of compounds A and B are shown in Figure 1. The pK_a values at variable ionic strengths and temperatures are shown in Table I. In A, pK_1 and pK_2 correspond to N1–H and C4–NH–Xy deprotonations, respectively. It can be seen that pK_1 and pK_2 values remain practically unaffected when ionic strength varies but a slightly decrease when temperature rises in the 20–40°C range. It is seen that pK_2 values of A are in a higher range than those corresponding to its unglycosidated homologue 4-amino-1,6-dihydro-2-methylthio-5-nitroso-6-oxo-

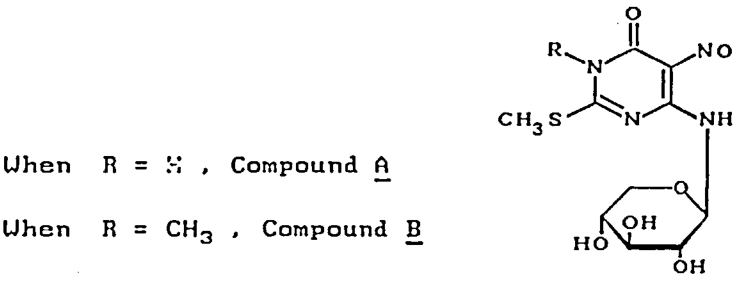

FIGURE 1 Schematic representation of compounds A (R=H) and B (R=CH_3).

TABLE I
Determined pK_A values for A and B at various ionic strengths (KCl) and temperatures.

		A		B
I(mol/L)	T(°C)	pK_1	pK_2	pK_1
0.01	25	6.50	10.85	10.80
0.03	25	6.49	10.86	10.90
0.06	25	6.48	10.87	10.82
0.10	25	6.47	10.89	10.85
0.20	25	6.46	10.89	11.02
0.10	20	6.56	11.03	10.95
0.10	30	6.47	10.72	10.77
0.10	35	6.43	10.57	10.62
0.10	40	6.38	10.43	10.42

pyrimidine;[14] this fact, also observed in other similar cases,[15,16] could be adscribed to the inductive effect of the glycosidic residue on the C4–NH group, which enhances the covalent character of the NH bond. As Log K_1 and I values, for compound A, follows the Debye-Hückel limiting equation, $\log K_a = \log K_t + c_t \sqrt{I}$ (where K_a represents apparent deprotonation constants and K_t the thermodynamic ones), we determined the K_t value corresponding to the first deprotonation process, $K_t = 3.09 \times 10^{-7}$. This value suggests that the N1-H group is easily deprotonated in polar solvents; moreover, pK_2 values, corresponding to deprotonation of the C4-NH group, are practically equal to those of compound B, which indicates the negative charge of anion A^- does not make more difficult. This fact is consistent with the hypothesis that the negative charge of A^- is located on the O atom of the C6–O group of the pyrimidine moiety.

Accordingly, it could be expected for A to be anionic in polar solvents, in which it would react with metal ions as a chelating agent through C-60–NO or N1–C6-0 bridges; nevertheless, the former would be preferred as it would lead to the formation of a stable five or six membered ring. On the contrary, it could be expected for B, in polar solvents, to act as a neutral ligand and consequently to display variability in its coordination mode.

IR and NMR data for A and B (Tables II and III, respectively), are in accordance with the tautomeric structures of Figure 1. Thus, IR spectra show two ν(NH) stretching vibration bands in the case of A and one in that of B, those being at 3260 and 3220 cm^{-1}, respectively, and corresponding to the C4–NH groups. All the remaining IR bands have been assigned previously.[15] Concerning ^{1}H NMR spectra of A, the signals corresponding to N1-H and C4–NH groups appear at 13.05 and 12.55 ppm, respectively; this assignment was made on the basis that the C4–NH signal (at 12.55 ppm) appears as a doublet due to its coupling with Cl'H of the sugar. The low field value of the C4–NH signal, in both A and B spectra, can be explained by the existence of an intramolecular hydrogen bond between the C4–NH group and the O atom of the adjacent C5–NO group. A list of the ^{13}C NMR signals of the two organic ligands are also included in Table III; accurate assignment could not be carried out, except in the case of the C5' signal (DEPT spectra).

Colours, analytical data and proposed formulae for the complexes are given in Table IV (water was determined by TG analyses). The complexes have ligand/metal stoichiometries of 1/1 or 2/1. The two Ag(I) complexes are insoluble in water and most common organic solvents, whereas $Co(A^-)_2.4H_2O$ is fairly soluble and the remaining ones highly soluble. TG curves of the complexes prove the hydrated character of all of them except for $Ag(B)(NO_3)$.[17] Dehydrations take place between 50–200°C before pyrolyses start, except in the case of $Cu(B^-)(NO_3).2H_2O$ where loss of water overlaps with the onset of pyrolytic decomposition.

IR and NMR results

Three of the A complexes have the organic ligand as the monoanion A^-, whereas in $Ni(A)_2(NO_3)_2.4H_2O$ the ligand acts as a neutral molecule. In accordance with that, the IR spectra of $Co(A^-)_2.4H_2O$, $Cu(A)NO_3.2H_2O$ and $Ag(A^-).2.5H_2O$ show the disappearance of the ν(C=O) band which indicates the negative charge of the anion A^- to be located on the O atom substituted at C6 of the pyrimidine ring; on the contrary, the ν(C=O) band is present in the IR spectrum of $Ni(A)_2(NO_3)_2.4H_2O$, although shifted 35 cm^{-1} to lower wavenumbers. Possible changes in ν(NH) bands could not be observed due to their overlap with the broad ν(OH) bands of water. The ^{1}H NMR spectra of the above three A^- complexes shows the disappearance of the N1-H signal (13.05 ppm in the free ligand), thus indicating the said group to be the one deprotonated. In spite of their low resolution, the ^{1}H NMR spectrum of $Ni(A)_2(NO_3^-).4H_2O$ is well resolved in the case of C4–NH and N1-H signals.

Two of the B complexes contain this ligand in molecular form, $Ni(B)_2(NO_3)_2.4H_2O$ and $Ag(B)(NO_3)$; and $Cu(B^-)(NO_3).2H_2O$ contains the monoanion, B^-. In accordance with this fact, IR spectra of Ni(II) and Ag(I) complexes with B show strong ν(C=O) bands at 1629 cm^{-1} (strongly shifted to lower wavenumbers) and 1692 cm^{-1} (unshifted), respectively. In the spectrum of the Cu(II) complex the strong ν(C=O) band disappears, but a new medium intensity one (assigned to $\nu(N{=}H)_{imino}$) arises at 1676 cm^{-1}. These facts, previously observed in similar cases,[15] indicate that with deprotonation of 4-NH-Xy, the negative charge of B^- is also located on a 6-Oxo group. NMR spectra of $Cu(B^-)(NO_3).2H_2O$ complex were not well resolved; on the contrary, ^{1}H NMR spectra of Ni(II) and Ag(I) complexes with B clearly show the presence of a signal at 12.30 and 12.20 ppm, respectively assigned to the 4-amino group; these bands appear as doublets due to their coupling with Cl'H. IR spectra of all of the complexes containing NO_3^- show a strong single band at 1384–1385 cm^{-1}

TABLE II
IR spectral data (cm^{-1}) for the ligands and complexes.

Compound	$\nu(OH)$	$\nu(NH)$	$\nu(CH)$	$\delta(OH_2)$	$\nu(C{=}O)$	$\nu(C_4{=}N)$	$\nu(C{=}C)+$ $+\nu(C{=}N)$	$\nu(NO)$	$\nu(NO_3^-)$
A	3399 m	3260 m-w 3090 m-w	3020 w 2920 w		1684 s	1558 s	1580 s	1484 m	
B	3374 s	3220 m-w	2899 w 3013 w		1692 s		1579 s 1540 s	1486 m	
$Co(A^-)_2.4H_2O$	3309 m, b	[a]	2923 w	1705 w			1540 s, m	1414 m	
$Ni(A)_2(NO_3)_2.4H_2O$	3352 s, b	[a]	2927 w 2867 w		1649 s		1561 s	1420 m	1384 s
$Cu(A^-)(NO_3).2H_2O$	3378 m, b	[a]	2969 w 2925 w				1572 s	1438 m	1385 s
$Ag(A^-).2.5H_2O$	3335 m, b	[a]	2919 w 2840 w	1724 w		1568 s	1463 m 1523 s		
$Ni(B)_2(NO_3)_2.4H_2O$	3449 s, b	[a]	2925 w 2855 w		1629 s		1592 s 1548 s	1411 sh	1385 s
$Cu(B^-)(NO_3).2H_2O$	3366 s, b		2924 w 2857 w			1676 m	1580 s 1535 m	1415 sh	1384 vs
$Ag(B)(NO_3)$	3378 s, b	3224 m, sh	2921 w 2850 w		1692 s		1583 s 1539 s	1486 m	1385 vs

[a] Masked by (OH) broad band; w, weak; m, medium; s, strong; b, broad; sh, shoulder; vs, very strong.

TABLE III
NMR data (in ppm) for ligands and complexes.

	^{1}H-NMR					^{13}C-NMR	
Compound	N1–H	N1–CH_3	C2–SMe	C4–NH	C1′H	Pyrimidine moiety	Glycosidic fragment
A	13.0		2.55	12.55^d	4.90–5.50^d	169.97; 160.62; 145.80; 142.21	81.10; 76.08; 72.13; 69.13; 67.26 (C5′)
A^-			2.55	12.40^d–4.90	4.80–5.80^b		
B		3.50	2.65	12.25^d	5.45^d	170.86; 160.27; 143.64; 142.27	81.02; 76.08; 72.01; 69.16; 67.23 (C5′)
$Co(A^-)_2.4H_2O$			2.55	9.55^d, 9.85^d	4.90–5.65^b	184.50^d; 177.75^d; 151–00^d; 135.80^d	signals between 66.74–87.55
$Ni(A)_2(NO_3)_2.4H_2O$	13.00			12.45			
$Cu(A^-)(NO_3).2H_2O$			2.55	7.60	^{b}	^{b}	^{b}
$Ag(A^-).2.5H_2O$			2.55	7.70	4.80–5.50^b	131.92; 128.54	
$Ni(B)_2(NO_3)_2.4H_2O$		3.50^c	2.65	12.30^d	4.80–5.60^b	170.79; 160.22; 143.69; 142.21	80.96; 75.98; 71.95; 69.10; 67.13
$Ag(B)(NO_3)$		3.50	2.70	12.20^d	^{b}	171.08; 160.35; 144.02; 142.08	81.03; 76.03; 71.98; 69.14; 67.21 (C5′)

[d] Doublet. [b] Not well resolved. [c] Overlaps with H_2O signal.

TABLE IV
Colour, analytical data (theoretical values in parentheses) and proposed formulae for the complexes.

Complex	Colour	Analytical data (%)				
		C	H	N	Metal	H_2O
$Co(A^-)_2.4H_2O$	orange	31.39 (31.29)	4.32 (4.43)	14.80 (14.60)	7.40 (7.70)	9.70 (9.41)
$Ni(A)_2(NO_3)_2.4H_2O$	green	27.84 (26.94)	4.19 (4.04)	15.09 (15.71)	6.72 (6.59)	8.48 (8.08)
$Cu(A^-)(NO_3).2H_2O$	green	25.21 (25.07)	3.56 (3.55)	13.51 (14.63)	12.95 (13.25)	7.47 (7.51)
$Ag(A^-).2.5H_2O$	dark green	24.85 (25.53)	3.71 (3.83)	11.32 (11.91)	23.19 (22.95)	9.81 (9.57)
$Ni(B)_2(NO_3)_2.4H_2O$	green	28.25 (28.73)	4.27 (4.35)	15.00 (15.23)	6.33 (6.39)	7.40 (7.84)
$Cu(B^-)(NO_3).2H_2O$	brown	26.34 (26.80)	3.82 (3.86)	13.95 (14.21)	12.62 (12.90)	[a]
$Ag(B)(NO_3)$	green	26.97 (26.30)	3.39 (3.19)	13.52 (13.94)	21.10 (21.49)	

[a] Dehydration overlaps with pyrolytic decomposition.

which proves that the said ions are not directly coordinated to the corresponding metal.[18]

The IR spectra of all of the complexes show the ν(NO) bands strongly shifted to lower wavenumbers with respect to the corresponding free ligands (except in that of $Ag(B)NO_3$ in which the band is practically unmodified), which points, to the implication of the C5–NO group in coordination to the metal ion. Thus, in those complexes having the organic ligand in the C6-oxo anionic form it could be expected that the corresponding organic ligands act as chelating agents through the C6-oxo and NO groups. Likewise, in the case of the two Ni(II) complexes, when the organic ligand acts as a neutral molecule, the strong shift to lower wavernumbers of ν(C=O) bands with respect to the corresponding free ligand (35 cm^{-1} in the case of $Ni(A)_2(NO_3)_2.4H_2O$ and 70 cm^{-1} in that the $Ni(B)_2(NO_3)_2.4H_2O$) may indicate that in these complexes 6-oxo groups are also implicated in coordination (C6=O—NO). On the contrary, IR, ^1H NMR and ^{13}C NMR spectra of $Ag(B)(NO_3)$ are very similar to those of B, which indicates that coordination takes place through the S–CH_3 group of the pyrimidine moiety. Thus, having in mind the insolubility of this compound, it could exist in a chain structure in which the bridging S atoms are coordinated to the two Ag atoms, as was observed by X-ray diffraction for the complex formed by 4,6-diamine-2-thiopyrimidine and Cd(II).[19]

A notable feature in the ^1H NMR spectra of complexes having A or B in the anionic form is the strong shift of the C4–NH signals to higher field (see Table III). Given that the ^1H NMR spectrum of A^- (obtained from NaA), shows the C4–NH signal at similar value as in the A spectrum, the feature is only attributable to the breaking of the hydrogen bridge between C4–NH and C5–NO groups. This implies that the organic ligand is in the configuration shown in Figure 2, so that the coordination sites would be the oxygen atoms of 6-oxo and NO groups, respectively. However, in the two Ni(II) complexes the C6–NH signal remains practically unaffected, which indicates that the hydrogen bond between C4–NH and C5–NO is present; having in mind this data together with the IR results, it is established that in the two Ni(II) complexes coordination takes place through the O atom of the 6-oxo group and the N atom of the C5-NO group (see Figure 3). Similar ^1H-NMR and IR features are found for the complex $Cd(AMNU)_2$ (where HAMNU is

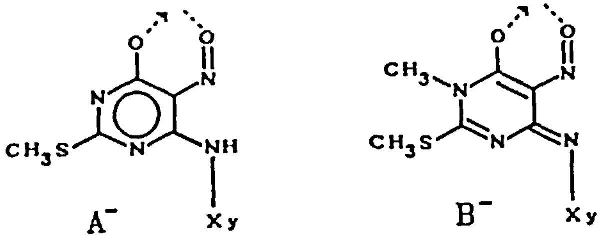

FIGURE 2 Schematic representation of the coordination of A^- and B^- in their metal complexes.

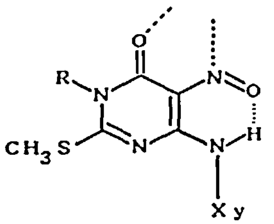

FIGURE 3 Schematic representation of the coordination of A and B in their Ni(II) complexes.

6-amino-3-methyl-5-nitrosouracil) whose molecular structure (in which hydrogen bonds are present) was established by X-ray diffraction.[20,21]

In agreement with all the above data, changes in chemical shift values of signals due to pyrimidine moities, in $Co(A^-)_2.4H_2O$ and $Ag(A^-)2.5H_2O$, are probably due to enhancement of aromaticity of the pyrimidine ring, arising when the N1–H group of the a molecule loses the H atom, thus giving rise to the 6-Oxo anion. As expected, those of the complexes having the organic ligand in the molecular form show ^{13}C NMR signals of the pyrimidine ring at similar field values to those of the free ligand (*i.e.*, $Ni(B)_2(NO_3)_2.4H_2O$ and $Ag(B)(NO_3)$). No noticeable changes were observed in the glycosidic range of the ^{13}C NMR spectra in those cases which showed good resolution. Accurate assignment of metal-donor atom bands in the IR spectra of the complexes was prevented because of strong ligand bands in the low frequency range.

Tentative structures

The magnetic moment for $Co(A^-)_2.4H_2O$ is 4.73 BM which suggests a probable tetrahedral arrangement. This fact implies that the water molecules are uncoordinated; this agrees with the low dehydration enthalpy of 15 kJ mol^{-1} for each water molecule).

The two Ni(II) complexes $Ni(A)_2(NO_3)_2.4H_2O$ and $Ni(B)_2(NO_3)_2.4H_2O$ have magnetic moments of 2.89 and 3.00 BM, respectively. These values are near the spin only moment in a d^8 system with two unpaired electrons, suggesting an octahedral arrangement around the Ni(II) ions. As discussed above, each organic ligand acts as bidentate; thus, two water molecules would probably be coordinated to the metal ions. Although the existence of coordinated water could not be proved by IR methods, TG and DSC data[17] agree with this hypothesis. The existence of an unsymmetrical endothermic effect corresponding to the dehydration of the compounds point to the

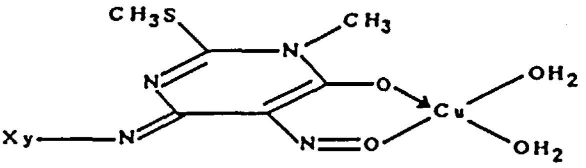

FIGURE 4 Proposed structure of Cu(B^-) $NO_3.2H_2O$.

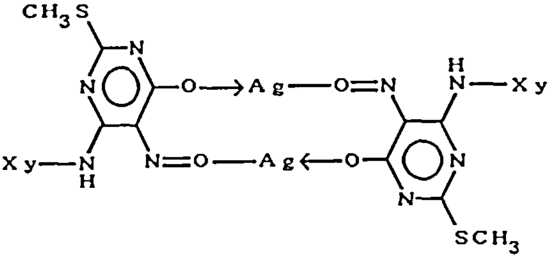

FIGURE 5 Proposed structure of Ag(A^-).$2.5H_2O$.

fact that the four water molecules are structurally inequivalent and mean dehydration enthalpies (38 and 40 kJ mol^{-1}, respectively) are significantly high.

Cu(A^-)$2H_2O(NO_3)$ has a magnetic moment of 1.20 BM which points to probable antiferromagnetic interactions, in accordance with square-planar or deformed tetrahedral structures in which A^- acts as a chelate with two water molecules coordinated to the Cu(II) ion; nevertheless, accurate integration of the dehydration endotherm could not be effected because it overlaps with an exothermic effect corresponding to combustion of the NO_3 group. In Cu(B^-)$2H_2O(NO_3)$, the dehydration enthalpy of 65 kJ mol^{-1} for each water molecule suggests that the two water molecules are coordinated to the Cu(II) ions. The magnetic moment for the complex is 2.05 BM which rules out any of Cu–Cu interactions. Thus the complex probably possesses a square-planar or deformed tetrahedral arrangement of the four donor atoms as shown in Figure 4.

Ag(A^-).$2.5H_2O$ is extremely unsoluble in most common solvents. The very low dehydration enthalphy (11 kJ mol^{-1}) suggests that the two water molecules are not directly linked to the Ag(I) ion. From this and the spectral data, a dimeric structure in which two Ag(I) ions are linked by two A^- anions, as shown in Figure 5, is proposed.

Electronic spectral data for the complexes, corresponding to the 240–1500 nm range, are summarized in Table V. All complexes show a strong band about 330 nm, which correspond to the π—π^* transition of the organic ligands. Cu(B^-)$2H_2O(NO_3)$, Cu(A^-)$2H_2O(NO_3)$ and Co(A^-)$_2$.$4H_2O$ exhibit strong charge-transfer bands; remaining features correspond to *d*—*d* transitions. The assignments and ranges in which the bands appear are in accordance with literature data for previously proposed structures.[22,23]

TABLE V
Electronic spectral data for the complexes.

Compound	λmax (nm)	Assignment
$Co(A^-)_2.4H_2O$	667	${}^4T_1(P) \rightarrow {}^4A_2$
	459 s	Charge-Transfer.
	342 s	$\pi^* \rightarrow \pi$ (ligand)
$Ni(A)_2(NO_3)_2.4H_2O$	836	${}^3T_{2g} \rightarrow {}^3A_{2g}$
	644	${}^3T_{2g}(F) \rightarrow {}^3A_{2g}$
	383 (sh)	${}^3T_{1g}(P) \rightarrow {}^3A_{2g}$
	323 s	$\pi^* \rightarrow \pi$ (ligand)
$Ni(B)_2(NO_3)_2.4H_2O$	875	${}^3T_{2g} \rightarrow {}^3A_{2g}$
	698	${}^3T_{1g}(F) \rightarrow {}^3A_{2g}$
	410	${}^3T_{1g}(P) \rightarrow {}^3A_{2g}$
	329	$\pi^* \rightarrow \pi$ (ligand)
$Cu(A^-)2H_2O(NO_3)$	700	d → d Transitions
	400 (sh), s	Charge Transfer
	340 s	$\pi^* \rightarrow \pi$ (ligand)
$Cu(B^-)2H_2O(NO_3)$	700–500[a] wi, u	d → d Transitions
	450 s	Charge Transfer
	325 s	$\pi^* \rightarrow \pi$ (ligand)

Sh; shoulder. wi; wide. u; unsimmetrical. [a] Overlaps with 450 nm bands; strong.

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