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Metal Complexes of Some 5-Nitrosopyrimidine Derivatives

G. Cruz-Bermúdez[a], A. García-Rodríguez[a], M. Moreno-Carretero[b], J. M. Salas-Peregrin[a,*], and C. Valenzuela-Calahorro[c]

[a] Department of Inorganic Chemistry, Faculty of Sciences, E-18071 Granada, Spain

[b] Department of Inorganic Chemistry, University College, E-23071 Jaen, Spain

[c] Department of Inorganic Chemistry, Faculty of Sciences, E-08071 Badajoz, Spain

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$M(ADNU)_2$ complexes [where M = Cu(II), Ni(II), Pd(II) and Pt(II); H*ADNU* = 6-amino-1,3-dimethyl-5-nitroso-uracil], $Co(ADNU)_3 \cdot 5\,H_2O$, $Pt(ADNU)_2Cl_2 \cdot 0.5\,H_2O$, $Pd(ADU)_2$ and $Pt(ADU)_2Cl_2$ (where H*ADU* = 1,3-dimethyl violuric acid) have been synthesized and characterized by elemental analysis, IR, magnetic measurements and thermal analysis (TG and DSC). All the isolated complexes of formulas $M(ADNU)_2$ or $M(ADU)_2$ show a square planar geometry, whereas the others are octahedral. Both ligands coordinate in bidentate form through the nitrogen and oxygen atoms of the 5-nitroso and 6-oxide groups.

(Keywords: Complexes; Uracil; Viouluric acid)

Metall-Komplexe einiger 5-Nitrosopyrimidine

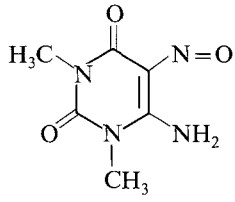
Komplexe des Typs $M(ADNU)_2$ [M = Cu(II), Ni(II), Pd(II), Pt(II); H*ADNU* = 6-Amino-1,3-dimethyl-5-nitroso-uracil], $Co(ADNU)_3 \cdot 5\,H_2O$, $Pt(ADNU)_2Cl_2 \cdot 0.5\,H_2O$, $Pd(ADU)_2$ und $Pt(ADU)_2Cl_2$ (mit H*ADU* = 1,3-dimethylviolursäure) wurden synthetisiert und mittels Elementaranalysen, IR, magnetischen Messungen und Thermoanalyse (TG und DSC) charakterisiert. Alle isolierten Komplexe der allgemeinen Formeln $M(ADNU)_2$ oder $M(ADU)_2$ waren von quadratisch planarer Geometrie, während die anderen sich als octaedrisch erwiesen. Beide Liganden komplexieren zweizähnig über die Stickstoff- und Sauerstoffatome der 5-Nitroso- und 6-Oxo-Gruppen.

Introduction

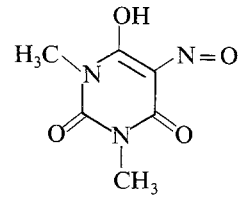
We have previously reported [1–13] that the interactions of some 5-nitrosopyrimidine derivatives with first row metal ions in aqueous

medium lead to the formation of a great number of complexes which have been characterized by spectroscopic and thermal methods. Most of these complexes involve a bidentate coordination mode through the exocyclic 5-nitroso and 6-oxo groups. This has been verified from X-ray studies carried out on Zn(II) and Cd(II) complexes with 6-amino-3-methyl-5-nitroso-uracil [14–15] and Cu(II) [16], Fe(II) [17], and Ag(I) [18] complexes of 1,3-dimethyl violuric acid.

In this context we report here the preparation and characterization of eight new metal complexes of 6-amino-1,3-dimethyl-5-nitroso-uracil (H*ADNU*) and 1,3-dimethyl violuric acid (H*ADU*).



H*ADNU*



H*ADU*

Experimental

6-amino-1,3-dimethyl-5-nitroso-uracil and 1,3-dimethyl violuric acid were prepared by methods previously reported [19–21]. All the chemical used in this work were analytical reagent grade.

The complexes were prepared as follows: A hot solution (100 ml) containing 1.5 mmol of the ligand was mixed, slowly with stirring, with a solution of the corresponding metallic chloride (0.75 mmol). In the case of Co(II) and Ni(II) complexes, ethanolic media were used, whereas the other compounds were obtained in aqueous solution. When the solutions were allowed to stand at room temperature, the compounds precipitate immediately. The Co(III) complex crystallizes from the solution obtained after the separation of the Co(II) compound.

All the complexes were filtered off, washed consecutively with water, ethanol and diethylether and air-dried. Their chemical analyses and colour are given in Table 1.

Chemical analysis of C, H and N were performed by means of microanalytical methods using a Perkin-Elmer 240 microanalyzer. Determination of metals was carried out by thermogravimetry. Infrared spectra were recorded in KBr pellets (4000–200 cm^{-1}) and in polyethylene pellets (600–200 cm^{-1}) on a Beckman 4250 spectrophotometer. TG studies were carried out on a Mettler TG-50 thermobalance using a heating rate of 20 °C min^{-1} and an air flow of 100 ml min^{-1}. The weight of samples was comprised between 5.62 and 18.05 mg. DSC runs were made on a Mettler DSC-20 differential scanning calorimeter using a static atmosphere of

air and a heating rate of 10 °C min^{-1} with samples varying in weight from 1.29 to 4.94 mg.

Magnetic measurements were carried out on a Bruker B-M 4 magnetic balance using the *Faraday* method. As standards $[Hg(SCN)_4]Co$ and $[Ni(en)_3]S_2O_3$ were used. Magnetic susceptibilities were obtained at room temperature and corrected for diamagnetism using the *Pascal* constants.

Table 1. *Analytical data of the isolated complexes (calculated values in parentheses)*

Compound	Colour	C(%)	H(%)	N(%)	*M*(%)
$Co(ADNU)_2$	Orange	33.57 (33.89)	3.26 (3.29)	25.82 (26.36)	12.31 (13.86)
$Co(ADNU)_3 \cdot 5H_2O$	Orange	30.27 (30.94)	4.32 (4.44)	23.89 (24.07)	7.68 (8.40)
$Ni(ADNU)_2$	Orange	33.84 (33.90)	3.02 (3.29)	26.49 (26.37)	13.07 (13.82)
$Pd(ADNU)_2$	Orange	30.42 (30.48)	3.02 (2.96)	23.64 (23.71)	21.43 (22.52)
$Pt(ADNU)_2$	Green	24.98 (25.67)	2.22 (2.49)	19.39 (19.96)	34.96 (34.76)
$Pt(ADNU)_2Cl_2 \cdot 0.5H_2O$	Green	22.30 (22.47)	2.18 (2.34)	17.66 (17.47)	32.56 (30.42)
$Pd(ADU)_2$	Orange	30.35 (30.35)	2.10 (2.53)	17.71 (17.70)	22.46 (22.43)
$Pt(ADU)_2Cl_2$	Yellow	23.01 (22.71)	1.75 (1.89)	13.11 (13.25)	30.81 (30.76)

Results and Discussion

In Table 1 the composition and colour of the isolated complexes obtained by reaction between H*ADNU* and H*ADU* with a number of metal ions have been collected. From this table it can be seen that, with exception of $Co(ADNU)_3 \cdot 5H_2O$, all the complexes show a 1:2 metal : ligand ratio.

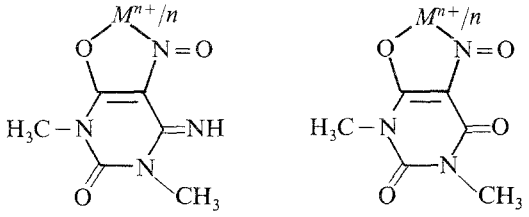
To establish the metal-ligand binding mode, we have only used IR techniques, since due to the low solubility of these compounds in several solvents, it has not been possible to record ^{1}H-NMR spectra.

Most important IR bands for the isolated complexes have been tabulated in Table 2. The assignments of these bands have been realized by comparison with those corresponding to the ligands [6, 22] and other analogous complexes previously described in the literature [1, 6, 9–11, 16, 23–25]. The position of these bands is in agreement with a coordination

Table 2. *IR data* (cm^{-1})

Compound	ν(O−H)	ν(N−H)	ν(C=O)	ν(C=N)	ν(C=C)	ν(N=O)	ν(C−O)
H*ADNU*	3 550	3 320	1 725	1 660	1 585	1 515	1 050
Co(*ADNU*)$_2$	—	3 310	1 715	1 660	1 600	1 505	1 075
Co(*ADNU*)$_3 \cdot 5\,H_2O$	3 440	—	1 715	1 665	1 600	1 510	1 080
Ni(*ADNU*)$_2$	—	3 320	1 710	1 660	1 580	1 505	1 080
Pd(*ADNU*)$_2$	—	3 360 3 310	1 715	1 670	1 580	1 500	1 080
Pt(*ADNU*)$_2$	—	3 300	1 715	1 675	1 590	1 510	1 080
Pt(*ADNU*)$_2$Cl$_2 \cdot 0.5\,H_2O$	3 470	3 300	1 715	1 670	1 585	1 510	1 080
H*ADU*	3 510 3 450	—	1 740 1 675	—	1 600	—	1 040
Pd(*ADU*)$_2$	—	—	1 715 1 665	—	1 560	1 510	1 085
Pt(*ADU*)$_2$Cl$_2$	—	—	1 735 1 680	—	1 550	1 500	1 060

mode of H*ADNU* and H*ADU* in imino-phenolic form through nitrogen and oxygen atoms of the 5-nitroso and 6-oxide groups, since all IR spectra show (in relation with the IR spectra of free ligands) a displacement to lower wavenumber of the band corresponding to $\nu(N=O)$ and a displacement to higher wavenumber of the $\nu(C-O)$ band. Both facts are according with the above mentionated coordination mode (Scheme 2) since this binding mode produces simultaneously a decrease in the double bond character of nitroso group and some double band character in the C_6-0 band, as a consequence of the electronic delocalization in the formed chelate ring.



This coordination type has been found from X-ray diffraction studies carried out on bis(4-amino-1,2-dihydro-1-methyl-5-nitroso-2-oxo-6-pyrimidinolato) diaqua cinc(II) dihydrate [14] and bis(1,3-dimethyl-2,4-dioxo-5-nitroso-1,2,3,4-tetrahydro-6-pyrimidinolato) diaqua copper(II) [16].

For $Pt(ADNU)_2Cl_2 \cdot 0.5\,H_2O$ and $Pt(ADU)_2Cl_2$ complexes, IR spectra show in the far region bands at $354\,cm^{-1}$ and $350\,cm^{-1}$, respectively, which are assignable to $\nu(Pt-Cl)$ the stretching mode [26].

Magnetic measurements carried out on these complexes have shown that all of them are diamagnetic, except the Co(II) complex, for which a 1.38 BM magnetic moment has been found. This permits to propose for $Co(ADNU)_3 \cdot 5\,H_2O$, $Pt(ADNU)_2Cl_2 \cdot 0.5\,H_2O$ and $Pt(ADU)_2Cl_2$ octahedral geometries whereas the other complexes seem be square-planar. The low value found for the magnetic moment of $Co(ADNU)_2$ can be explained by existence of metal-metal interactions.

In Table 3 the most important features found in the thermal studies of these complexes are summarised. The thermal decomposition of complexes with general formula ML_2 takes place in two steps corresponding to the pyrolitic degradation of the samples and are reflected in the DSC curves by exothermic effects. For hydrated and halogenated compounds a dehydration or dehalogenation process takes place before pyrolitic degradation.

Table 3. *Thermoanalytical data*

Compound	Process	Temperature range TG (°C)	DSC peak temperature (°C)	Accumulated weight loss (%)		Residue
				Found	Calcd.	
$Co(ADNU)_2$	Pyrolysis	320–430	375 (exo), 420 (exo)	83.2	81.12	Co_3O_4
$Co(ADNU)_3 \cdot 5\,H_2O$	Dehydration	60–140	108 (endo)	12.2	12.80	
	Pyrolysis	290–550	340 (exo), 420 (exo), 480 (exo)	89.5	88.60	Co_3O_4
$Ni(ADNU)_2$	Pyrolysis	320–440	>400 (exo)	83.1	82.50	NiO
$Pd(ADNU)_2$	Pyrolysis	350–450	380 (exo), >440 (exo)	75.3	74.09	PdO
$Pt(ADNU)_2$	Pyrolysis	300–430	350 (exo), >440 (exo)	65.04	65.24	Pt
$Pt(ADNU)_2Cl_2 \cdot 0.5\,H_2O$	Dehydration	140–160	157 (endo)	1.9	1.40	
	Dehalogenation	290–320	[a]	11.5	12.46	
	Pyrolysis	320–420	360 (exo)	67.4	69.58	Pt
$Pd(ADU)_2$	Pyrolysis	310–380	360 (exo)	74.2	74.20	PdO
$Pt(ADU)_2Cl_2$	Dehalogenation	290–320	300 (exo)	11.9	11.18	
	Pyrolysis	320–415	380 (exo), >440 (exo)	69.2	69.24	Pt

[a] This peak is overlapping with those associated with the pyrolytic process

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