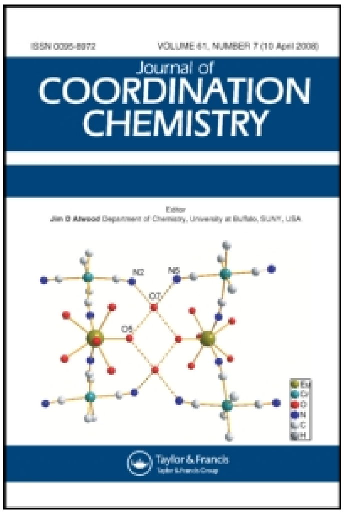

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Communication the First Examples of the Coordination Ability of 9-OXO-10-Acridineacetic Ion, an Important Interferon Inducer

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COMMUNICATION

THE FIRST EXAMPLES OF THE COORDINATION ABILITY OF 9-OXO-10-ACRIDINEACETIC ION, AN IMPORTANT INTERFERON INDUCER

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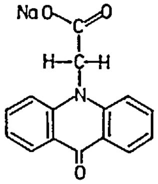
9-Oxo-10-acridineacetic acid, CMA, has been found to be an interferon inducer.[1-5] Moreover, it has been shown that some analogues of CMA may significantly enhance the titres of serum interferon in mice. Among them, the sodium salt CMANa, (I), was synthesized and its biological activity was recently analysed.[6] This work presents the results of a study on the interaction of CMA$^-$ with Co(II), Ni(II), Cu(II), and Zn(II).

Keywords: 9-Oxo-10-acridineacetic acid, complexes, characterization, first row



EXPERIMENTAL

CMANa was prepared by the published method.[6] The isotopes ^{62}Ni, ^{58}Ni, ^{65}Cu, ^{63}Cu were purchased from Techsnabexport SU. The purity of the isotopes was above 90%.

Warm water solutions of CMANa (0.0015 mol) were added to warm water solutions of metal chloride (M=Ni, Co) or metal sulphate (M=Cu, Zn) (0.0005 mol). The solutions were heated and stirred for two hours when solid crystalline complexes were obtained. The complexes of CMANa with ^{62}Ni(II), ^{58}Ni(II), ^{65}Cu(II) and ^{63}Cu(II) were prepared by the same way as above, on milligram scale. The precipitates were filtered, washed and dried in vacuum.

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Electronic spectra were measured on a Hitachi 365 spectrophotometer, and IR spectra on Perkin-Elmer 621 and Perkin-Elmer 180 instruments using standard techniques. The ESR spectrum was obtained on a JEOL EPR JES Me 3X spectrometer. An F. Paulik, J. Paulik, L. Erday 342 T derivatograph was used for obtaining thermal data.

RESULTS AND DISCUSSION

The results of elemental analyses are in a good agreement with the formulae $[NiL_2(H_2O)_2].2H_2O$, $[CoL_2(H_2O)_2].2H_2O$, $[CuL_2(H_2O)_2]$ and $[ZnL_2(H_2O)_2].2H_2O$. The presence of both coordinated and crystalline water in the Co, Ni and Zn complexes was indicated by their IR spectra.

Both diffuse reflectance and solution (formamide) spectra were recorded to assign stereochemical configurations in the complexes. As the solid state and solution spectra are roughly the same, we suggest the preservation of the M–O arrangement in both states.

In the visible region of the $CuL_2(H_2O)_2$ spectrum one broad asymmetric band at 14200 cm^{-1} with an extinction coefficient of 49 M^{-1}cm^{-1} is observed. It probably results from a tetragonally distorted octahedral Cu(II) ion. Because electronic spectra can often be insensitive to the detailed nature of the distortion of the O_h symmetry in Cu(II) complexes, an ESR study has been made. $[CuL_2(H_2O)_2]$ shows an axial ESR spectrum characteristic for monomeric compounds. The values of $g_\perp$ and $g_\parallel$ ($g_\perp = 2.093$ and $g_\parallel = 2.335$) fall in the range typical for a slightly distorted O_h configuration.[7,8]

TABLE I

The CT transitions for CMANa and its complexes [cm^{-1}], (ε = dm^2 mol^{-1} × 10^{-3}).

Complex	ν(ε)	ν(ε)
$[NiL_2(H_2O)_2] \times 2H_2O$	24560 (15.1)	25640 (13.7)
	32570 (2.55)	33900 (4.7)
$[CoL_2(H_2O)_2] \times 2H_2O$	24500 (17.3)	25640 (15.6)
	32680 (2.8)	33780 (5.4)
$CuL_2(H_2O)_2$	24510 (17.7)	25640 (16.0)
	32570 (3.2)	33900 (5.8)
$[ZnL_2(H_2O)_2] \times 2H_2O$	24630 (16.2)	25640 (14.5)
	32470 (3.5)	33900 (4.5)
CMANa	24630 (7.7)	25710 (7.0)
	32570 (1.5)	34010 (2.7)

In the electronic absorption region of $[NiL_2(H_2O)_2]\cdot 2H_2O$, we observe three bands due to d–d transitions (absorption coefficients, M^{-1}cm^{-1}, in parentheses) at 8620 cm^{-1} (3.78) $^3A_{2g} \rightarrow {}^3T_{2g}$, 13660 cm^{-1} (4.2) $^3A_{2g} \rightarrow {}^3T_{1g}$, and 14925 cm^{-1} (4.3) $^3A_{2g} \rightarrow {}^1E_g$. From the position of the bands the ligand field parameters 10 Dq and B are calculated to be 8620 cm^{-1} and 649 cm^{-1}, respectively. These results show that the nickel ion possesses O_h configuration, which can be slightly distorted in the MO_4O_2' type complex.[9,10] In the electronic absorption spectrum of the Co(II) complex, two d–d transitions are found at 15380 cm^{-1} (1.3)sh $^4T_{2g} \rightarrow {}^4A_{1g}$, and a structured multiplet at 19270 cm^{-1} (25.6) $^4T_{2g} \rightarrow {}^4T_{1g}$ (P). The ligand field par-

TABLE II

Main IR bands and assignments [cm^{-1}] for the ligand and complexes[a].

Compound	H_2O coord.	$\nu(CO_2)_{asym.}$	$\nu(CO_2)_{sym.}$	Δ_1	$\nu(M{-}O)_{MO_4}$	Δ_2	$\nu(M{-}O)_{MO_4}$	Δ_3	$\nu(M{-}O)_{H_2O}$	Δ_4	H_2O "free"
CMANa		1555 s	1392 s	163							3510,3470 s
$[NiL_2(H_2O)_2] \times 2H_2O$	3200–3050 s	1572 s	1400 s	172	292 m	2	345 m	2	386 s	4	3480 m
$[CoL_2(H_2O)_2] \times 2H_2O$	3200–3050 s	1575 s	1390 s	185	284 m		346 m		387 s		3510 m
$CuL_2(H_2O)_2$	3200–3050 s	1572 s	1395 s	177	278 m	3	350 s	1	398 s	1	
$[ZnL_2(H_2O)_2] \times 2H_2O$	3200–3050 s	1562 s	1397 s	165	260 m		327 s		387 s		3440,3380 s

[a] Abbreviations: s = strong, m = medium; $\Delta_1 = \nu(CO_2)_{asym.} - \nu(CO_2)_{sym.}$ $\Delta_{2,3,4} = \nu([^{58}NiL_2(H_2O)_2] \times 2H_2O) - \nu([^{62}NiL_2(H_2O)_2] \times 2H_2O)$. $\Delta_{2,3,4} = \nu(^{63}CuL_2(H_2O)_2) - \nu(^{65}CuL_2(H_2O)_2)$ for the metal–oxygen vibrations.

ameters 10 Dq and B are 8225 cm^{-1} and 878 cm^{-1}, respectively. From these results and known data for six-coordinate cobalt complexes with oxygen donor ligands, a pseudo-octahedral symmetry is proposed.[9,10]

Table I gives the positions and the values of ε for bands observed in the region of ligand absorption for CMANa and all the complexes studied. The results indicate a significant enhancement of absorption intensities in the spectra of the complexes with respect to the ligand.

The main IR bands in the spectra of CMANa and its complexes are listed in Table II. A strong, broad band observed in the region 3200–3000 cm^{-1} in the spectra of all the complexes is certainly due to the absorption of the coordinated water.[11,12] The value of $\Delta = \nu_{asym}(CO_2) - \nu_{sym}(CO_2)$ observed for the complexes lies in the range 158–185 cm^{-1}, whereas it is equal to 163 cm^{-1} for the 9-oxo-10-acridineacetic anion. For such a value of Δ, both chelating or bridging acetate groups can be predicted.[13] The precise nature of $-COO^-$ group bonding can only be revealed by use of X-ray methods.

In the FIR region the bands appearing in the spectra of the complexes have been assigned to metal–oxygen vibrations, according to the isotopic shifts observed (Table II). The band positions are typical for octahedrally coordinated ions.[11,12,14,15]

The absorptions located near 3500 cm^{-1} in the spectra of the ligand, $[NiL_2(H_2O)_2].2H_2O$, $[CoL_2(H_2O)_2].2H_2O$ and $[ZnL_2(H_2O)_2].2H_2O$ cannot be assigned unequivocally. McKenzie has observed similar bands in the IR region for 1,7-bis-2-pyridyl-2-6-diazaheptanecopper(II) and palladium(II) perchlorate and has assigned them to "free" water molecule vibrations.[16,17] The presence of water in the cobalt complex is supported by the results of thermal analysis. However, this method gives only its total amounts, equal to 10% by weight, and in accord with the proposed formulae.

This study of the molecular arrangement around the metal ions is a first step in the detailed characterization of the complexing ability of CMA^-, a powerful interferon inducer. The evaluation of stability constants as well as further studies of CMA complexes could be helpful for an understanding of the biological activity of the ligand. Attempts are currently being made to grow single crystals suitable for X-ray crystallographic determinations.

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