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Communication

MOLECULAR COMPLEXES OF SOME NEW AZO-8-HYDROXYQUINOLINE SULPHONAMIDE METAL CHELATES WITH PICRIC ACID

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Two heterocyclic derivatives of azo-8-hydroxyquinoline sulphonamides and their metal complexes were synthesized. The complexes form the respective molecular complexes with picric acid. All the compounds were characterized on the basis of elemental analysis and spectral measurements.

INTRODUCTION

In view of the biological importance of sulphonamide derivatives a considerable work on this class of compounds and their metal complexes¹⁻³ has been made. Further, the donor behavior of 8-hydroxyquinoline and some of its complexes with organic acceptors such as 1,3,5-trinitrobenzene, chloranil, picryl azide, benzotrifurazan, and 7,7,8,8-tetracyanoquinodimethane is known in the literature.⁴⁻⁸ The present study deals with the preparation of two azo-8-hydroxyquinoline sulphonamides, namely 4-[8-hydroxy-5-quinolylazo]benzenesulphonamyl morpholine and 4-[8-hydroxy-5-quinolylazo]benzenesulphonamyl 2-aminopyridine and their complexes with Co⁺², Ni⁺², and Hg⁺², which interact with picric acid to afford molecular complexes of some interest.

RESULTS AND DISCUSSION

The complexes are obtained according to the following reactions:

$$MCl_2.nH_2O + 2L \longrightarrow ML_2 + 2HC1 + nH_2O$$

$$2ML_2 + Pic \longrightarrow (ML_2)_2.Pic$$

$$M = Co(II), Ni(II) or Hg(II)$$

$$n = O or Co$$

$$Pic = picric acid$$

$$L = Ligand: HQAMo, HQAPy$$

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	C (Calc.)	H (Calc.)	N (Calc.)
НОАМо	(57.27)	(4.55)	(14.06)
C ₁₉ H ₁₈ N ₄ O ₄ S	57.88	4.59	14.17
[Co(HQAMo) ₂]	(53.46)	(4.01)	(13.12)
CoC38H34N808S2	53,55	4,17	13.01
[Co(HQAMo)2]2.Pic	(50.85)	(3.69)	(13.74)
Co2C82H71N19023S4	50.73	3.60	13.66
[Ni(HQAMo) ₂]	(53.47)	(4.01)	(13.12)
N1C38H34N808S2	53.53	4.16	13.00
[Ni(HQAMo),],.Pic	(50.87)	(3.69)	(13.74)
N12 ^C 82 ^H 71 ^N 19 ⁰ 23 ^S 4	50.72	3.53	13.82
[Hg(HQAMo) ₂]	(45.85)	(3.44)	(11.25)
HgC38H34N808S2	45.95	3,53	11.19
[Hg(HQAMo) ₂] ₂ .Pic	(44.36)	(3.22)	(11.98)
Hg2 ^C 82 ^H 71 ^N 19 ⁰ 23 ^S 4	44.22	3.11	11.87
HQAPy	(59.25)	(3.72)	(17.27)
C ₂₀ H ₁₅ N ₅ O ₃ S	59.37	3.61	17.39
[Hg(HQAPy) ₂]	(47.59)	(2.79)	(13.87)
HgC40H28N1006S2	47.41	2.88	13.70
[Hg(HQAPy) ₂] ₂ .Pic	(45.95)	(2,64)	(14.33)
Hg ₂ C ₈₆ H ₅₉ N ₂₃ O ₁₉ S ₄	45.81	2.73	14.49

Abbreviations: HQAMo = 4- 8-hydroxy-5-quinolylazo benzene sulphonamyl morpholine.

HQAPy: 4- 8-hydroxy-5-quinolylazo benzene sulphonamyl-2-aminopyridine.

Pic = Picric acid.

The analytical data of the complexes are tabulated in Table I. The complexes are fairly soluble in chloroform, acetone and alcohol. A change of color from brown-red to red was noticed upon the addition of picric acid to the metal chelates.

The electronic spectra of the prepared metal azo-8-hydroxyquinolinate derivatives in chloroform solutions are generally characterized by bands due charge transfer $(L \rightarrow M)$ and intraligand transitions.

The d-d bands of the Co(II) and Ni(II) complexes are obscured by these transitions. The close similarity between the electronic spectra of the complexes and those of related compounds⁹ indicate the tetrahedral structure around the metal ions. The prepared molecular complexes show new bands in the range 310-430 nm which can be attributed to charge transfer transitions. It is to be noted that this range is also exhibited by some related compounds⁷ and by an adduct of nickel (II) oxinate with methanol.¹⁰ It was reported that in certain types of mixed ligand complexes the electronic transitions involving charge transfer from ligand to ligand are possible to occur. The corresponding absorption bands may be seen at low energies if one ligand possesses high-lying filled orbitals (MOMO) and the other low-lying empty orbitals (LUMO).¹¹ In our molecular complexes one can suggest that the metal orbitals have a contribution to the charge transfer process in combination with the ligands π -electrons. An extension of the π -electrons from the metal chelate to the picric acid through hydrogen bonding is thus assumed to occur.

The IR spectra of the metal chelates (Table II) indicate the disappearance of

TABLE II

IR (cm⁻¹) and electronic (nm) spectral data of the ligands and their complexes

Compound			IR			UV-VIS
	. v0H	vCN	∨N=N	vNO _{as}	vNO _s	λ _{max}
HQAMo	3250	1650	1580	-	-	470,395,270
[Co(HQAMo) ₂]	-	1630	1580	-	-	465,345,310
[Co(HQAMo) ₂] ₂ .pic	-	1620	1580	1530	1340	470,420,330
[N1(HQAMo) ₂] ₂	-	1630	1550	-	-	480,410,260
[Ni(HQAMo) ₂] ₂ .pic	-	1620	1560	1530	1340	480,430,340
Hg(HQAMo) ₂	-	1620	1550	1530	1340	490,445,325
[Hg(HQAMo) ₂] ₂ .pic	-	1630	1560	1530	1345	480,430,330,275
HQAPy	3260	1660	1550	-	-	475,395,270
[Hg(HQAPy) ₂]	-	1630	1540	-	_	395,315,270
[Hg(HQAPy) ₂] ₂ .pic	-	1630	1530	-	1340	395,330,270

 ν OH and the shift of ν C = N to a lower frequency (1620-1660 cm⁻¹); a behavior which confirms coordination of the metal ions to the 8-hydroxyquinoline moiety. Furthermore, the molecular complexes exhibit ν N = Oas and ν N = Os of picric acid at 1530 and 1340-1345 cm⁻¹, respectively. They are shifted from their positions in picric acid. 12 ν C = N and ν N = N are shown at almost the same frequencies as in the prepared metal azo-8-hydroxyquinolines. The following structure can be proposed for the molecular complexes:

EXPERIMENTAL

All chemicals and solvents were analytical grade. The electronic spectra were obtained by a Shimadzu UV-200S spectrophotometer and the IR spectra in KBr pellets were measured using a Perkin-Elmer 599B spectrophotometer.

The ligands were prepared by the diazotisation of the free p-aminobenzene sulphonyl derivatives and then coupling with 8-hydroxyquinoline in acetic acid medium at 0°C.

The complexes were precipitated when mixing the alcoholic solutions of the ligands and the metal chloride salts in the molar ratio 2:1 under continuous stirring.

The molecular complexes were obtained by refluxing a suspension of the metal oxinate derivatives with a benzene solution of picric acid. The red products, which precipitated by cooling the benzene layer, were collected, filtered and washed with little benzene and dried.

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