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MAGNETIC AND SPECTRAL STUDIES OF MIXED LIGAND DERIVATIVE OF COBALT(II) β-DIKETONATE AND β-DIKETOESTERS WITH 8-HYDROXY QUINOLINE

Introduction

β-DIKETONE and β-diketoester exhibit keto-enol tautomerism, react with metal cations to form complexes, which behave as Lewis acids and form adducts with Lewis bases. As the complexes of β-diketoesters closely resemble those of β-diketonates, a study of the reaction of 8-hydroxyquinoline with bis(acetylacetonato), bis(methylacetoacetato) and bis(ethylacetoacetato) cobalt(II) was undertaken.

Experimental

The diaquo-bis(acetylacetonato), bis(methylacetoacetato) and bis(ethylacetoacetato) Co(II) were prepared by the general method, by adding the respective ammonical solutions of acetylacetone, methylacetoacetate and ethylacetoacetate (0·02 mole) in ethanol to a solution of cobalt chloride-6-hydrate (0·01 mole) in ethanol-water with constant stirring. The separated cobalt(II) derivatives were filtered, washed with water and dried *in vacuo*.

Stoichiometric amount of 8-hydroxyquinoline (0·01 mole) dissolved in the minimum volume of ethanol was added to the corresponding solution of cobalt(II) β-diketonate and β-diketoester (0·01 mole) dissolved in ethanol and the resulting solution was refluxed for 15 min. The yellow microcrystals of the solid, separated out, was filtered, washed with ethanol and dried *in vacuo*. The purity of the isolated products was established by elemental analyses. Analytical data agreed with the composition of the complex within the limits of experimental errors.

The magnetic measurements were carried out using Gouy's method in pyridine solution at $300° \pm 1°$ K, electronic spectra were taken in pyridine solution on a Carl Zeiss Jena VSU2-P spectrophotometer, while I.R. spectra were recorded as nujol mull on Perkin Elmer Model-577. These mixed ligand complexes are soluble in pyridine and do not melt upto 350° C.

Discussion

In divalent cobalt, there are three *d-d* transitions[1] arising from the ground state $^4T_{1g}$ (F) to $^4T_{2g}$, $^4A_{2g}$ and $^4T_{1g}$ (P) states in weak field and are denoted as ν_1, ν_2 and ν_3. The band ν_3 occurs as a shoulder in the region 20000–22000 cm^{-1}, while the band ν_2 occurs as a broad band in the region 18400–19600 cm^{-1}, corresponding to the band $\sim$ 20000 cm^{-1} and at 17850 cm^{-1} in octahedral hexaaquocobalt(II) ion[1] respectively. The lower energy band ν_1 lies in the region 8600–8900 cm^{-1} corresponding to a band at 8350 cm^{-1} in aquo complex. The pattern of electronic spectra of these complexes have been found to be similar to hexaaquocobalt(II) ion suggesting thereby that the stereochemistry of metal ion of both the species are almost identical. The lower values for nephelauxetic ratio β, in these mixed ligand complexes as compared to their respective parent complexes, indicate the increase in covalency. The values for Racah interelectronic repulsion parameter[2] B, crystal field splitting energy 10Dq and β have been summarized in Table I.

TABLE I

Calculated values for parameter B, 10Dq (in cm^{-1}), β and significant IR bands (in cm^{-1})

Complex	B	β	10 Dq	ν (C–O)	ν (C–C)	ν (M–O)
Co (AcAc)$_2$ (H$_2$O)$_2$	961·5	0·989	10991	1517	1600	422
Co (AcAc)$_2$ (8-HQu)	919·1	0·945	10373	1525	1608	430
Co (MeAcAc)$_2$ (H$_2$O)$_2$	960·8	0·988	10913	1620	1505	450
Co (MeAcAc)$_2$ (8-HQu)	899·1	0·925	10206	1625	1518	455
Co (EtAcAc)$_2$ (H$_2$O)$_2$	963·2	0·991	10719	1626	1525	480
Co (EtAcAc)$_2$ (8-HQu)	895·5	0·920	10209	1632	1535	485

The value of magnetic moment (μ_{eff}) of these complexes are in the range of 5·05 to 5·19 BM.[3], suggesting the presence of three unpaired electrons and hence the complexes are spin-free with octahedral stereochemistry.

The infrared spectrum of the parent complexes has confirmed the presence of coordinated water molecules $\sim$ 3,450 cm^{-1}, while the complexes derived from 8-hydroxyquinoline do not show absorption in this region. This indicates that these mixed ligand complexes are anhydrous. The significant bands ν(C–N) and ν(C–O) due to coordinated 8-hydroxyquinoline occurs around 1590 cm^{-1} and 1095 cm^{-1} respectively[4]. The bands ν(C–O), ν(C–C) and ν(M–O) due to coordinated acetylacetone[5], methylacetoacetate and ethylacetoacetate[6] have been given in Table I.

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D. S. SANKHLA.
O. P. ARORA.
SUDHINDRA N. MISRA.*

* For correspondence.

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5-SUBSTITUTED-1, 3, 4-THIADIAZOLYL-2-DITHIOCARBAMYL-(N,N,N-TRIALKYL) ETHYL AMMONIUM IODIDES AS ANTI-ACETYL-CHOLINESTERASES

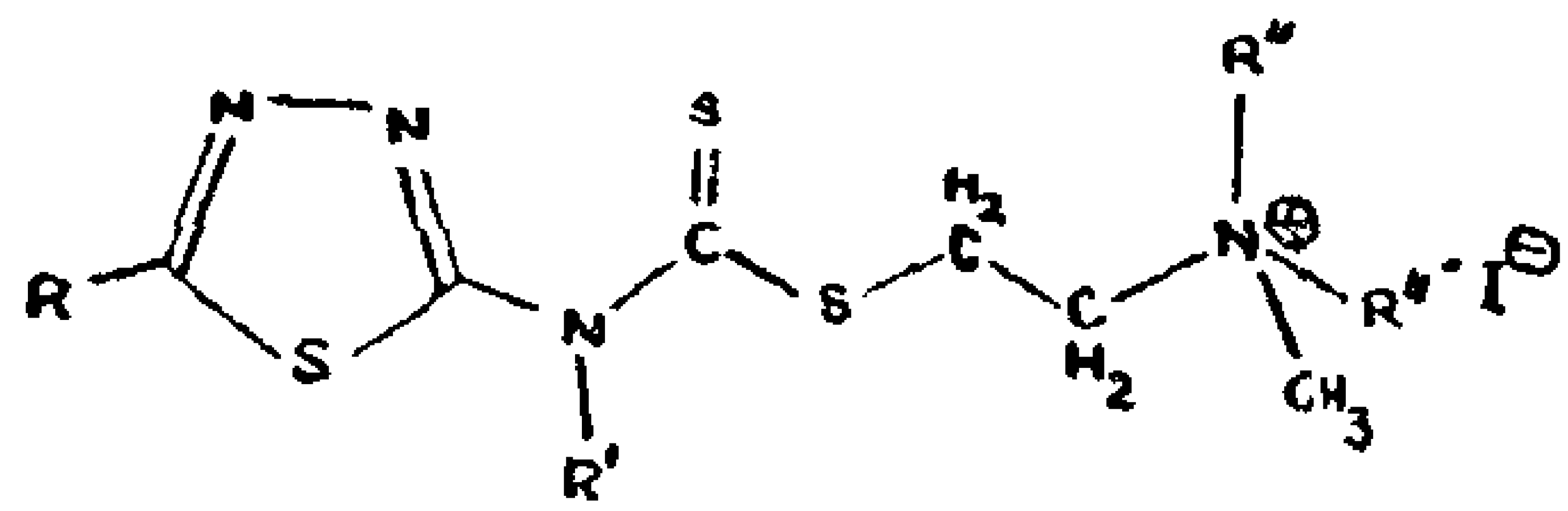
QUATERNARY ammonium salts have been found active as cholinergics[1] as well as anti-cholinergics[2,3]. In the last communication[4], a few title compounds were described to be the CNS excitants. This indicated a cholinergic mechanism of action of these quaternary ammonium compounds on the central nervous system of mice. To substantiate this observation, the title compounds have been screened out for anti-acetyl-cholinesterase activity on isolated brain tissues of rats. The compounds have been found to possess good anti-acetyl-cholinesterase activity.

The method of Parmar *et al*[5] was adopted to estimate anti-acetyl-cholinesterase activity of the compounds. The substrate used was acetyl-thiocholine iodide. The 'sulfhydryl' content of the thiocholine, liberated after enzymatic hydrolysis, was determined colorimetrically in a spectrophotometer at a wavelength of 520 mμ. The reduction in the 'Sulfhydryl' content, when the title compounds took part in the reaction, marked the anti-acetyl-cholinesterase activity of the test compounds.

The anti-acetyl-cholinesterase activity of the title compounds are listed in Table I.

TABLE I

Anti-acetyl-cholinesterase activity of 5-substituted-1, 3, 4-thiadiazolyl-2-dithiocarbamyl-(N, N, N-trialkyl)- ethyl ammonium iodides



Sl. No.	R	R′	R″	Anti-acetyl-cholin-esterase activity (% inhibition)
1.	–H	$-CH_3$	$-CH_3$	55
2.	$-CH_3$	$-CH_3$	$-CH_3$	50
3.	$-C_2H_5$	$-CH_3$	$-CH_3$	42
4.	–n·C_3H_7	$-CH_3$	$-CH_3$	35
5.	–n·C_4H_9	$-CH_3$	$-CH_3$	34
6.	$-C_6H_5$	$-CH_3$	$-CH_3$	25
7.	$-SCH_3$	$-C_6H_5$	$-CH_3$	25
8.	$-SCH_3$	o–$CH_3.C_6H_4$–	$-CH_3$	25
9.	$-SCH_3$	m–$CH_3.C_6H_4$–	$-CH_3$	51
10.	$-SCH_3$	p–$CH_3.C_6H_4$–	$-CH_3$	66
11.	$-C_6H_5$	$-CH_3$	$-C_2H_5$	25
12.	$-SCH_3$	$-C_6H_5$	$-C_2H_5$	28
13.	$-SCH_3$	o–$CH_3.C_6H_4$–	$-C_2H_5$	30
14.	$-SCH_3$	m–$CH_3.C_6H_4$–	$-C_2H_5$	64
15.	$-SCH_3$	p–$CH_3.C_6H_4$–	$-C_2H_5$	85