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Coordination Compounds of Hydrazine Derivatives with Transition Metals. VIII. Copper(II) Complexes with Salicylaldehyde and Acetylacetone Aroylhydrazones.

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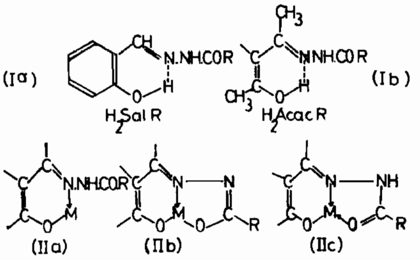
Copper(II) chelates of salicylaldehyde aroylhydrazones [H_2Sal-R] and acetylacetone aroylhydrazones [H_2Acac-R] have been prepared. Elemental analyses, infrared and electronic spectra as well as the magnetic susceptibility measurements are used for their characterisation. A distorted square pyramidal structure is tentatively assigned for chelates of the type [Cu(H Sal-R)Cl·X] (X = H_2O or pyridine), whereas the anhydrous chelates [Cu(H Sal-R)Cl] possess square planar arrangement with the chloride ion occupying a coordination site. In both types the hydrazone molecule acts as a monobasic tridentate ligand. The neutral chelates [Cu(Sal-R)] and [Cu(Acac-R)], on the other hand, possess subnormal magnetic moments and may achieve square planar structure through molecular association. In these chelates, the hydrazone molecule acts as a dibasic tridentate ligand. Their interaction with pyridine afforded the monomeric monopyridinate adducts.

Introduction

It was previously reported that studies on coordination properties of aroylhydrazones and their aromatic Schiff bases, specially those derived from salicylaldehyde may provide a reasonable model for the mechanism of amine oxidase inhibition by many hydrazine derivatives[1]. In part III[2] of this series benzaldehyde aroylhydrazones were reported to act either as a neutral or monobasic bidentate ligands. Their reaction with copper(II) and nickel(II) acetates gave the bis neutral chelates with deprotonation of the imino hydrogen. With nickel chloride, on the other hand, the reaction afforded the dichloro-bis(aroylhydrazone)nickel(II) chelates in which the hydrazone molecules acted as neutral ligands. However, with copper(II) chloride the reaction proceeded through the reduction of copper (II) ions and the mono(aroylhydrazone)copper(I) monochloride complexes were isolated[2].

Aroylhydrazones of *ortho*-hydroxyaldehydes and ketones possess a third potent coordination site which makes them tridentate ligands[3,4]. Studies on the reaction of salicylaldehyde aroyl or acylhydrazones with nickel(II) or copper(II) salts showed that this type of ligands can either act as monobasic bidentate (II a) or dibasic tridentate molecules (II b).



The present work is devoted to study in some detail the interaction of copper(II) salts with aroylhydrazones derived from both salicylaldehyde (Ia) and acetylacetone (Ib) to gain more information about (i) the different modes of coordination of such ligands, (ii) the stereochemistry of the corresponding copper(II) chelates and (iii) the effect of the *ortho*-hydroxyl group on the reduction of copper(II) ions as compared with the previously reported benzaldehyde aroylhydrazones.

Results and Discussion

The reaction of salicylaldehyde aroylhydrazones [H_2Sal-R] (Ia, R = CH_3, C_6H_5 and p-$CH_3OC_6H_4$) with copper(II) chloride dihydrate in ethanol gave the hydrated monochloro chelates [Cu(HSal-R)Cl·H_2O] while with the corresponding *o*-hydroxy and *p*-nitrobenzoylhydrazones only the anhydrous chelates [Cu (HSal-R)Cl] were isolated. However, treatment of copper acetate dihydrate with the hydrazones (Ia, R = CH_3, C_6H_5, p-$NO_2C_6H_4$ and o-HOC_6H_4) in boiling ethanol afforded the mono neutral chelates of stoichiometry [Cu(Sal-R)]. Both [Cu(HSal-R)Cl] and [Cu(Sal-R)] are readily soluble in pyridine giving

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deep green solutions from which the monopyridinates [Cu(HSal-R)Cl·Py] and [Cu(Sal-R)·Py] were isolated, respectively.

All the copper(II) chelates of acetylacetone aroylhydrazones H_2Acac-R were prepared *in situ*. In boiling ethanol, the reaction of copper(II) acetate dihydrate with equimolecular mixture of the aroylhydrazines (NH_2NHCOR, R $=p$-$CH_3OC_6H_4$, p-$NO_2C_6H_4$ and o-HOC_6H_4) and acetylacetone yielded the mono neutral chelates of the formula [Cu(Acac-R)]. However, with benzoylhydrazine (R = C_6H_5), the reaction gave a brown chelate of the general formula [Cu(Acac-C_6H_5)Bz] where Bz refers to the neutral benzoylhydrazine molecule. Attempts to prepare monochloro chelates of the type [Cu(HAcac-R)Cl], by using copper(II) chloride instead of copper acetate were unsuccessful, but instead the neutral chelates [Cu(Acac-R)] were isolated.

Monochloro Copper(II) Complexes

The room temperature magnetic measurements (Table I) reveal that complexes of the type [Cu(HSal-R)Cl], [Cu(HSal-R)Cl·H_2O] and [Cu(HSal-R)Cl·Py] are paramagnetic with magnetic moments ($\simeq$1.8 BM) usually reported for magnetically diluted copper(II) chelates[5].

The infrared spectra of these chelates show maximum absorption bands due to N–H stretching, amide I band ν(C=O), azomethine stretching ν(C=N) and amide II band [6,7]. The positions of these bands are listed in Table II. Both the amide I and azomethine bands are located at lower frequencies as compared with the parent ligands. The infrared spectral data together with the stoichiometry of these chelates are in good agreement with the structure (IIc) in which the hydrazone molecule acts as monobasic tridentate ligand. In the infrared spectra of the monohydrates [Cu(HSal-R)Cl·H_2O] the O–H stretching mode appears as an intense doublet in the 3400–3320 cm^{-1} region, while the HOH deformation mode appears as a well defined band at about 1600 cm^{-1}. These bands are relatively sharp compared with the broad unresolved

TABLE I. Analytical and Magnetic Data of the Prepared Copper(II) Chelates.

Compound	Copper %		Nitrogen %		Chloride %		μ_{eff} (°K)
	Calc.	Found	Calc.	Found	Calc.	Found	
Copper(II) chelates of the type Cu(HSal-R)Cl							
Cu(HSal-C_6H_5)Cl·H_2O	17.84	17.85	7.83	7.83	9.95	9.63	1.81(299)
Cu(HSal-C_6H_5)Cl	18.79	18.80	8.28	8.02	10.48	10.03	1.80(299)
Cu(HSal-p-$CH_3OC_6H_4$)Cl·H_2O	16.46	16.32	10.23	10.12	9.18	9.26	1.82(300)
Cu(HSal-p-$NO_2C_6H_4$)Cl	16.50	16.40	10.96	10.96	9.28	9.59	1.82(300)
Cu(HSal-o-HOC_6H_4)Cl	17.89	17.76	7.91	7.87	10.72	10.54	1.81(300)
Copper(II) chelates of the type Cu(Sal-R)							
Cu(sal-C_6H_5)	21.00	21.25	9.28	9.35			1.38(300)
Cu(Sal-p-$CH_3OC_6H_4$)	19.10	19.30	8.44	8.42			1.39(300)
Cu(Sal-p-$NO_2C_6H_4$)	18.25	18.80	12.11	12.01			1.48(298)
Cu(Sal-o-HOC_6H_4)	20.01	20.12	8.81	8.71			1.33(301)
Copper(II) chelates of the type Cu(HSal-R)Cl·Py							
Cu(HSal-C_6H_5)Cl·Py	15.21	15.29	10.07	9.82	8.50	8.50	1.81(299)
Cu(HSal-o-HOC_6H_4)Cl·Py	14.60	14.53	9.69	9.53	8.18	7.72	1.82(299)
Copper(II) chelates of the type Cu(Sal-R)Py							
Cu(Sal-C_6H_5)Py	16.65	16.65	11.03	10.92			1.81(300)
Cu(Sal-p-$CH_3OC_6H_4$)Py	15.47	15.60	7.87	7.87			1.81(300)
Cu(Sal-p-$NO_2C_6H_4$)Py	14.81	14.54	13.13	12.89			1.80(300)
Cu(Sal-o-HOC_6H_4)Py	16.08	16.30	10.59	10.47			1.82(300)
Copper(II) chelates of the type Cu(Acac-R)							
Cu(Acac-C_6H_5)Bz	15.25	15.33	13.47	13.53			2.00(303)
Cu(Acac-p-$CH_3OC_6H_4$)	20.52	21.03	9.04	8.85			
Cu(Acac-p-$NO_2C_6H_4$)	19.57	19.69	12.94	12.75			1.49(303)
Cu(Acac)-o-HOC_6H_4)	21.49	21.36	9.47	9.21			1.50(300)
Copper(II) chelates of the type Cu(Acac-R)Py							
Cu(Acac-p-$NO_2C_6H_4$)Py	13.26	13.05	13.87	13.65			1.81(300)
Cu(Acac-o-HOC_6H_4)Py	16.96	16.67	11.21	11.00			1.82(300)

TABLE II. Infrared Spectral Data of Copper(II) Chelates.[a]

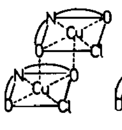
Compound	H_2O asym	H_2O sym	ν(N–H)	Amide I ν(C=O)	ν(C=N)	Conj. phenyl	Phenyl + Amide II		ν(C–O)
Organic ligands:									
H_2Sal-C_6H_5	–	–	3300 m	1680 s	1635	1605	1580 s	1570 s	1535 s
H_2Sal-*p*-$CH_3OC_6H_4$	–	–	3200 m	1675 s	1640 s	1600	1580		1520
H_2Sal-*p*-$NO_2C_6H_4$	–	–	3220 m	1670 s	1640 s	1620	1580 sh	1570 s	1540 s
H_2Sal-*o*-HOC_6H_4	–	–	3200 m	1670 sh	1630 s	1595	1580 m	1550 sh	1530 sh
H_2Sal-CH_3	–	–	3200 m	1685 s	1635 s	1605	1580 m	1550 m	1535 s
Copper(II) chelates of the type Cu(HSal-R)Cl									
Cu(HSal-C_6H_5)Cl·H_2O	3450	3350	3120 m	1615 s		1600 s	1585 sh	1550 m	1535 sh
Cu(HSal-C_6H_5)Cl	–	–	3125 m	1615 s	1605 sh	1590 sh			
Cu(HSal-*p*-$CH_3OC_6H_4$) Cl·H_2O	3450	3350	3200 m	1620 s	1605 sh	1590 m		1550 m	1520 m
Cu(HSal-*p*-$CH_3OC_6H_4$)Cl	–	–	3195 m	1620 s	1605 s	1590 sh		1560 m	1520 s
Cu(HSal-*o*-HOC_6H_4)Cl	–	–	3140 m	1620	1610 sh	1600	1580		1520 s
Cu(HSal-CH_3)Cl·H_2O	3450 b	–	3200 m	1630 s	1610 s	1600 s		1565 s	1525 s
Copper(II) chelates of the type Cu(Sal-R)									
Cu(Sal-C_6H_5)	–	–	–	–	–	1640 s	1590 sh	1565 m	1530 s
Cu(Sal-*p*-$CH_3OC_6H_4$)	–	–	–	–	1635 s	1605 s	1585 sh		1535 s
Cu(Sal-*p*-$NO_2C_6H_4$)	–	–	–	–	1630 s	1605 s			1535 s
Cu(Sal-*o*-HOC_6H_4)	–	–	–	–	1635 s	1600 s	1585 sh	1560 m	1530
Copper(II) chelates of the type Cu(Acac-R)									
Cu(Acac-*p*-$CH_3OC_6H_4$)	–	–	–	–	1615 s		1590		1530 s
Cu(Acac-*p*-$NO_2C_6H_4$)	–	–	–	–	1620 s	1600			
Cu(Acac-*o*-HOC_6H_4)	–	–	–	–	1620	1600			1530

[a] s = strong; m = medium; sh = shoulder; b = broad.

absorption usually observed in compounds containing lattice water[8].

Dehydration of the green monohydrates gave the brown anhydrous chelates. Differential thermal analyses reveal one definite exothermic peak at 157° C. Similarly the green monopyridinates [Cu(HSal-R)Cl·Py] were completely depyridinated on heating for three hours at 100° C under vacuum, giving also the brown anhydrous chelates. The above evidences suggest that both water and pyridine molecules occupy one site of coordination around the central copper(II) ion in [Cu(HSal-R)Cl·H_2O] and [Cu(HSal-R)Cl·Py] respectively.

The nujol mull electronic spectra of the anhydrous chelates (Table III) show a broad split shoulder extending from 14.0 to 16.0 kK. The spectra are in good agreement with those reported for copper(II) ion in square planar environments[9–13]. It is expected from the magnetic moments of these chelates that no appreciable intermolecular interaction would take place. However, the polymerised structure (III) cannot be ruled out, since normal magnetic moments were also reported for some copper(II) chelates with dimeric structures[14].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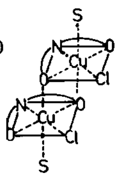
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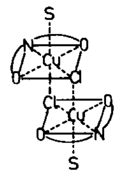
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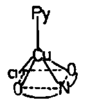

(V)

The spectra of the solid [Cu(HSal-R)Cl·H_2O] and [Cu(HSal-R)Cl·Py], on the other hand, are found to be essentially the same, but show different features as compared with those of the anhydrous chelates. The spectra, in general, display a split band with maxima at $\simeq$ 15 and 14.5 kK with evidence of shoulder at higher ($\simeq$18 kK) and lower ($\simeq$12.5 kK) energy sides. These spectral data could account for either five[15–19] or six coordinate geometry[20,21]. The latter may be achieved by dimerisation either through phenolic oxygen (IVa) or chloride bridge (IVb). Here again, the normal values of the magnetic moments of these chelates do not indicate any type of association and a monomeric structure (V) with five coordinate arrangement around copper(II) ions is most likely proposed

TABLE III. The Electronic Spectra of Copper(II) Chelates.[a]

Compound	State	Band Maxima, kK				(ε mol^{-1} l^{-1} cm^{-1})
$Cu(HSal-C_6H_5)Cl \cdot H_2O$	M			18.52		15.75, 14.05, 12.90sh
$Cu(HSal-C_6H_5)Cl \cdot Py$	M			19.00		15.63, 14.00sh, 10.30sh
$Cu(HSal-C_6H_5)Cl$	Py					15.63b(128), 10.26sh
$Cu(HSal\text{-}p\text{-}CH_3OC_6H_4)Cl \cdot H_2O$	M			18.20bsh		15.62sh, 15.04, 14.10sh, 13.31sh
	Py					15.75b(126), 11.20sh
$Cu(HSal\text{-}p\text{-}NO_2C_6H_4)Cl$	M	23.80	22.73	21.41sh		15.63b, 14.29sh, 13.10sh
	Py			18.35sh		15.46(126), 11.11sh
$Cu(HSal\text{-}o\text{-}HOC_6H_4)Cl$	M	25.00sh				15.27, 14.39, 13.13sh
	Py					15.40b(128), 9.96(24)
$Cu(HSal\text{-}o\text{-}HOC_6H_4)Cl \cdot Py$	M					15.50, 14.00sh, 9.88sh
$Cu(Sal-C_6H_5)$	M				16.95	15.04 sh
	Py					15.63b(145)
$Cu(Sal\text{-}p\text{-}CH_3OC_6H_4)$	M				16.26	15.15sh
	Py					15.20b(135)
$Cu(Sal\text{-}p\text{-}NO_2C_6H_4)$	M		22.99	21.51sh	16.67	15.50sh
	Py					15.38b(134), 11.90sh, 11.12sh
$Cu(Sal\text{-}o\text{-}HOC_6H_4)$	M					16.95, 14.77
	Py		22.73sh			15.50(134)
$Cu(Acac\text{-}p\text{-}CH_3OC_6H_4)$	M					16.00, 14.00sh
	Py			21.98sh		15.51b(108)
$Cu(Acac\text{-}p\text{-}NO_2C_6H_4)$	M		22.00sh	17.55sh		15.27, 13.99sh
	Py			21.74sh		16.00(225), 14.39bsh
$Cu(Acac\text{-}o\text{-}HOC_6H_4)$	M			18.18sh		15.75, 14.77sh
	Py					13.52(63), 12.74(44)

[a] M = nujol mull, Py = solution spectra in pyridine, b = broad, sh = shoulder.

for these chelates. Hathaway *et al.*[18,19] reported that five coordinate copper(II) complexes have a single rather intense band at *ca.* 15.0–18.0 kK and 12.0 kK for square pyramidal and trigonal bipyramidal arrangements, respectively. Splitting of the band, however, was frequently observed[15,16]. The spectra of both $[Cu(HSal-R)Cl \cdot H_2O]$ and $[Cu(HSal-R)Cl \cdot Py]$ are most probably related to copper(II) chelates with square based pyramidal stereochemistry. The splitting of the band and the presence of a well defined shoulder at$\simeq$12.5 kK may be taken as evidence for a distortion from idealized symmetry. Furthermore, the green solutions of the brown anhydrous chelates [Cu(HSal-R)Cl] in pyridine were found to be nonconducting. Their spectra (Table III) are identical with the nujol mull spectra of the solid monopyridinates $[Cu(HSal-R)Cl \cdot Py]$. Both the position and intensity of the bands are compatible with a distorted square pyramidal[15,18–21] rather than octahedral environment[20,21] around the copper(II) ion. These results may suggest that in neat pyridine only the five coordinate mono adduct (V) is formed with chloride ion occupying a site in the coordination polyhedron. The failure of the mono chloro chelate to give six coordinate species in pyridine solution may be related to the distorion of the square pyramidal structure. The copper(II) ion probably lies above the plane of the four coordination sites forming the base of the pyramid[22].

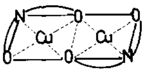
The Neutral Chelates [Cu(Sal-R)] and [Cu(Acac-R)]

The infrared spectra of these types of complexes (Table II) are completely different from those of the parent ligands. They lack any absorption due to N–H stretching, amide I and amide II bands, instead a very strong sharp band at 1630 cm^{-1} is developed. This band can be correlated to the stretching vibration mode of the conjugate C=N–N=C system. Such behaviour is diagnostic of the enolisation of the hydrazone residue[2].

The magnetic moments of the neutral chelates [Cu(Sal-R)] and [Cu(Acac-R)] are listed in Table I. The subnormal magnetic moments of the neutral chelates strongly suggest molecular association[23–26]. The degree of such an association cannot be assigned since no molecular weight determination was attempted due to their insolubility. The magnetic moments of their pyridine mono adducts, however, were within the normal range expected for magnetically non-interacting systems.

The nujol mull electronic spectra of the neutral chelates are similar to those of the corresponding pyridine mono adducts. The spectra (Table III) show a multicomponent band system covering the range 17.0–14.0 kK besides a strong charge transfer band at 21.0 kK. The general features of the spectra are consistent with square planar structure[9–13] and are rather similar to the spectra published for copper(II) chelates with many dibasic tridentate Schiff base ligands[26].

As is often proposed[26–29] for copper(II) chelates with dibasic tridentate ligands, the neutral chelates [Cu(Sal-R)] and [Cu(Acac-R)] may attain the four coordinate planar structure presumably by the dimerisation of two tricoordinate copper(II) units through oxygen bridges. Two dimeric structures are thus possible for these complexes, either with bridged phenolic or with hydrazide oxygen. The band located at about 1520 cm^{-1} in the infrared spectra of the parent ligands H_2Sal-R may be attributed to the phenolic C–O stretching[30]. Although the assignment of this band is not completely confirmed, a shift of 10–20 cm^{-1} to higher frequencies is certainly diagnostic of the formation of binuclear complexes with phenolic oxygen bridges[24]. In the infrared spectra of the neutral chelates [Cu (Sal-R)], this band does not show any higher frequency shift as compared with the parent ligands. These results imply the formation of hydrazide oxygen bridge and the dimeric structure (VI) may tentatively be assigned for these neutral chelates.


(VI)

Dissolution of the dimeric neutral chelates [Cu (Sal-R)] and [Cu(Acac-R)] in pyridine results in the destruction of the oxygen bridge and from these solutions the solid mono pyridinates [Cu(Sal-R)Py] and [Cu(Acac-R)Py] were respectively isolated. The magnetic and the electronic spectral data are in good agreement with square planar structure in which the pyridine molecule occupies the fourth coordination site around the copper(II) ion. The solution spectra of the neutral chelates in neat pyridine, however, are completely different from the mull spectra of the solid mono pyridinates. Such spectral changes suggest further interaction with pyridine molecules.

Conclusions

The reaction of both H_2Sal-R and H_2Acac-R with copper(II) salts yield the copper(II) chelates in which the H_2Sal-R molecule acts either as mono- or dibasic tridentate ligand, while H_2Acac-R molecule reacts only as dibasic tridentate ligand. Contrary to the behaviour of the bidentate aroylhydrazones[2] no reduction of copper(II) ion was detected. The presence of a third coordination centre in the hydrazone molecule may stabilize the copper(II) state.

The coordination properties of H_2Sal-R with copper (II) ion are compatible with those reported with N-salicylidene α-aminoacids[31,32]. The latter compounds were usually taken as a model molecule to understand several biochemical reactions catalysed by pyridoxal[33]. The inhibition of these reactions with aroyl or acylhydrazines may be due to the blocking of the pyridoxal formyl group with the formation of a stable pyridoxal aroylhydrazone copper(II) chelates analogous to [Cu(Sal-R)]. The aroyl- or acylhydrazine molecule, thus, may act as an α-aminoacid antagonist.

Experimental

Preparation of Organic Ligands

Aroyl- and acylhydrazines

These were generally prepared by the reaction of hydrazine hydrate with the corresponding ester[1].

N-salicylidene aroyl- or acylhydrazines

A solution of salicylaldehyde (0.02 mol) in ethanol (30 ml) was refluxed for 25 minutes with a solution of the aroyl- or acylhydrazine (0.02 mol) in methanol (30 ml). The hydrazones which separated on cooling were filtered, washed with ethanol and then dried over P_2O_5.

Preparation of Copper(II) Chelates

Mono(N-salicylidenato-aroylhydrazine)copper(II) monochloride complexes [Cu(HSal-R)Cl]

A solution of copper(II) chloride dihydrate (0.01 mol) in ethanol (25 ml) was treated with a hot solution of N-salicylidene aroylhydrazine (0.01 mol) in ethanol (30 ml). The reaction mixture was then refluxed for 25 minutes. On cooling the precipitated crystalline [Cu(HSal-R)Cl] complex was filtered, washed successively with ethanol and ether and then dried *in vacuo* over P_2O_5.

Mono(N-salicylidenato-aroylhydrazinato)copper(II) complexes [Cu(Sal-R)]

Method A A solution of aroylhydrazine (0.01 mol) in absolute ethanol (30 ml) was added with constant stirring to a suspension of salicylaldehyde copper(II) complex (0.01 mol) in absolute ethanol (20 ml) and the reaction mixture was refluxed for one hour. On cooling, the separated green [Cu(Sal-R)] complex was filtered, washed several times with ethanol and ether and then dried in a vacuum desiccator over P_2O_5.

Method B A hot solution of N-salicylidene aroylhydrazine (0.01 mol) in ethanol (30 ml) was added with constant stirring to a boiling solution of copper (II) acetate dihydrate (0.01 mol) in 60% aqueous ethanol (30 ml). The reaction mixture was then refluxed for 1.5 hours. On cooling, the desired product which separated was filtered, washed with boiling ethanol and then dried in a vacuum desiccator over P_2O_5.

Pyridine adducts of mono(N-salicylidene aroylhydrazinato)copper(II) complexes [Cu(R-Sal)Py]

The neutral copper(II) chelate [Cu(Sal-R)] (2 g) was dissolved in boiling pyridine (10 ml). The resulting deep green solution was filtered hot to which hot dry benzene (30 ml) was added. On cooling, the mono pyridine adduct which separated was filtered, washed with benzene and ether and then dried on water pump.

Pyridine adducts of mono(N-salicylidene aroylhydrazine)copper(II) monochloride [Cu(HSal-R)Py]

These adducts were prepared using the same procedure described for the preparation of the [Cu(Sal-R) Py] chelates.

Mono(acetylacetone aroylhydrazonato)copper(II) chelates [Cu(Acac-R)]

A solution of aroylhydrazine (0.01 mol) in absolute ethanol (30 ml) was added to a suspension of bis (acetylacetonato)copper(II) complex (0.01 mol) in absolute ethanol (20 ml). The reaction mixture was refluxed for one hour. On cooling, the green [Cu (Acac-R)] chelate was separated which was washed several times with ethanol and ether and dried *in vacuo* over P_2O_5.

Pyridine adducts of mono(acetylacetone aroylhydrazinato)copper(II) chelates [Cu(Acac-R)Py]

These adducts were prepared using the same procedure described for the preparation of [Cu(Sal-R)Py].

Analyses

The copper(II) content of the prepared complexes was determined by EDTA titration using pyridineazonaphthol (PAN) as indicator[34]. The nitrogen and chloride analyses were carried out at the Microanalysis Laboratory, Faculty of Science, Alexandria University. The results are given in Table I.

Physical Measurements

Magnetic and spectral data were obtained using the same procedures previously described[2]. Thermogravemetric and differential thermal analysis were performed on a Derivatograph Model D 102 manufactured by MOM (Hungary) using Al_2O_3 as standard.

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