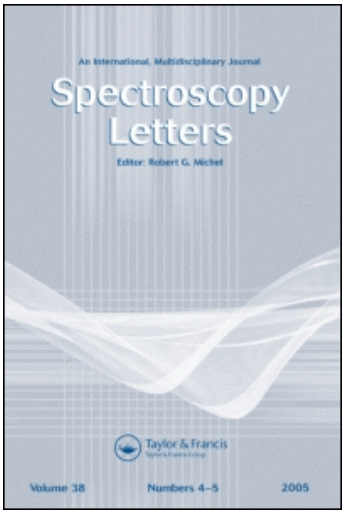


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

ESR Study of the Brown - form of Some Copper (II) Aroylhydrazone Complexes

S. Hedewy[a]
[a] Faculty of Sciences, University of Riyad, Saudi Arabia

To cite this Article Hedewy, S.(1979) 'ESR Study of the Brown - form of Some Copper (II) Aroylhydrazone Complexes', Spectroscopy Letters, 12: 6, 439 — 444
To link to this Article: DOI: 10.1080/00387017908069170
URL: http://dx.doi.org/10.1080/00387017908069170

SPECTROSCOPY LETTERS, 12(6), 439-444 (1979)

ESR STUDY OF THE BROWN - FORM OF SOME COPPER (II) AROYLHYDRAZONE COMPLEXES

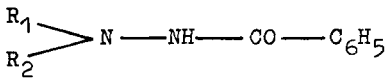
S.Hedewy

Faculty of Sciences , University of Riyad , Saudi Arabia

ESR study of the brown - modification of some copper (II) - aroylhydrazone complexes revealed a reduction in the type of polycrystalline spectra which have been noticed for the corresponding green - form complexes. The estimated values of both magnetic susceptibility and magnetic moment were less than those for the green chelates.

1. INTRODUCTION

Two modifications of copper (II) - aroylhydrazone complexes (green and brown) were isolated as a result of the reaction of copper acetate with ligands :



(R_1 , R_2 ; H , C_6H_5 ; H , p-CH_3.C_6H_4 ; H , p-CH_3O.C_6H_4 and H , p-Cl.C_6H_4) . ESR study of the green - form have been reported previously[1]. The aim of this work is to extend this study to include the brown - form chelates .

2. EXPERIMENTAL

X - band spectra were recorded using Varian E - 12 spectrometer . Dimethyl - formamide (DMF) was used as a solvent due to insolubility of the complexes in the previously used solvents (toluene and chloroform) .

3. RESULTS and DISCUSSION

An observable reduction in the type of polycrystalline spectra have been noticed for the brown chelates . Instead of the three g - factor spectrum observed for the green form of complex (II) , resulting from exchange interaction between misaligned tetragonal axes , the corresponding brown modification exhibited axial spectrum with two principal g - values indicating strictly parallel alignment of symmetry axes of the local copper (II) ion environment in the unit cell .

On the other hand , the brown form of complexes (I) , (III), and (IV) showed nearly an isotropic spectrum with a single g-value consisting of an asymmetrical line, due to the perpendicular part of the spectrum, but absorption due to the parallel spectrum was not detected although a sufficient gain have been used in this orientation . The line width of these asymmetrical lines showed negligable change at liquid nitrogen temperature . The observed g - values and line widths for the brown chelates under study are given in Table (1) .

Spin - spin interactions affect the line width either as broadening (dipole - dipole interaction) , or as narrowing (exchange interaction) . For purely dipolar interactions

Table(1)

Complex	R_1	R_2	g	ΔH
I	H	C_6H_5	2.13	92
II	H	p-$CH_3O.C_6H_4$	2.198 2.028	not measurable
III	H	p-$CH_3.C_6H_4$	2.14	60
IV	H	p-$Cl.C_6H_4$	2.17	45

between identical spins in field of cubic symmetry , the expected line width for polycrystalline powders is given by the expressions[2]

$$\langle \Delta H^2 \rangle = 3/5\ S\ (\ S + 1\ )\ g^2\ \beta^2\ \frac{8.5}{r^6}$$

and,

$$\Delta H_{dd} = 2.35\ [\Delta H^2\ ]^{1/2}$$

where r is the distance between the neighbouring spins .

For complexes under investigation, there are no informations in the literature about the crystal structure . However, if the observed linewidths were attributed to the dipolar interaction alone, then the estimated distances between neighbouring spins in the three complexes I , III , and IV amount the values 9.7 A^o, 11 A^o, and 12.2 A^o respectively which may be large for such complexes, indicating the existence of exchange narrowing . Such a predication was assured from the analysis of the line shape by the method described by Prew Swarup[3] which indicated an approach to the Lorentzian[4,5] shape.

Solution spectra of these complexes in DMF revealed only the metal quartet hyperfine structure with smearing of

nitrogen splittings which were observed in the case of the green complexes . The estimated values of both molar magnetic susceptibility $\chi_{av.}$ and magnetic moment $\mu_{av.}$ using the expressions:

$$\chi_{av.} = N \beta^2 g_o^2 S (S + 1) / 3KT$$

$$\mu_{av.} = \beta g_o \sqrt{S (S + 1)}$$

showed slight less values copared with those of the corresponding green complexes. As it is clear from Table (2) , these values are still within the normal range for copper complexes.

Dissimilar to the green form of complex (IV), where the frozen solution spectrum indicated an approach of copper (II) - ion during the freezing process forming ionic clusters with ionic concentration $n \gtrsim 10$, the corresponding brown modification exhibited at 77°K the spectrum illustrated in Fig.(1) which is

Table (2)

Complex	Brown - modifaction				Green - modifaction(1)			
	g_o	$a \times 10^4 cm^{-1}$	$\chi_{av.} 10^6$	$\mu_{av.}$	g_o	$a \times 10^4 cm^{-1}$	$\chi_{av.} 10^6$	$\mu_{av.}$
I	2.067	78.0	1359.65	1.794	2.096	73.4	1372.75	1.811
II	2.082	76.9	1363.60	1.799	2.102	72.2	1380.62	1.817
III	2.089	73.7	1368.2	1.805	2.099	71.0	1376.69	1.810
IV	2.092	70.3	1370.13	1.808	2.095	73.8	1371.44	1.810

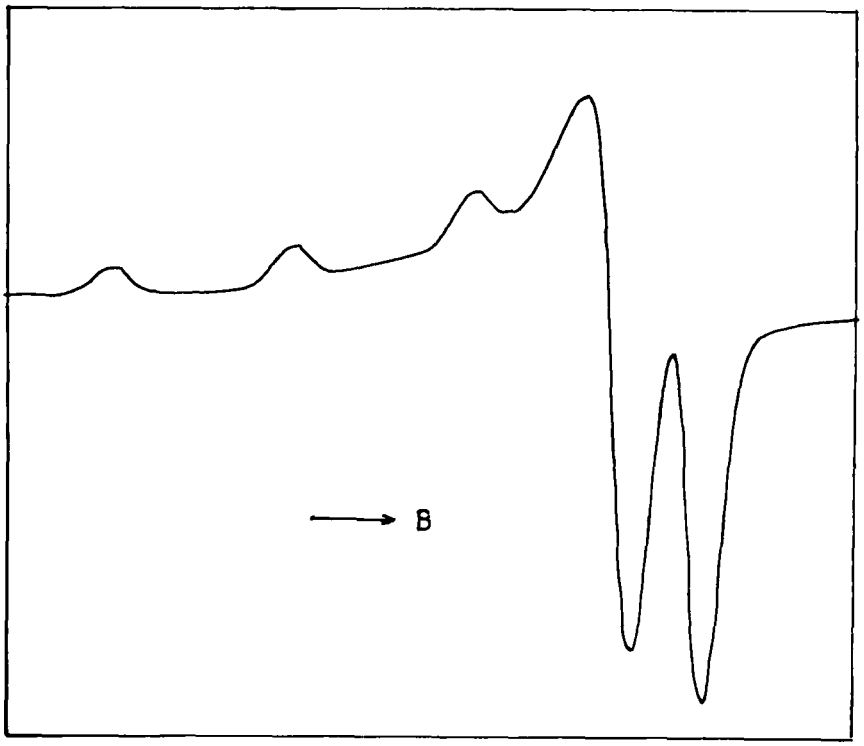


Fig.(1) Frozen solution spectrum of complex (IV)

Table (3)

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$	$A_{\perp}$	α^2
I	2.200	2.023	175.00	29.5	0.744
II	2.213	2.030	173.49	28.6	0.760
III	2.217	2.036	172.20	24.5	0.767
IV	2.220	2.043	170.10	20.44	0.770

typical of simply complexed copper (II) ions in frozen solutions. The line width of the first line in the lowest field , $\langle \Delta H \rangle$, defined as 0.3 times the distance from the center of the first peak to the skirt , which equals 13 gauss , denotes low ionic concentration ($n \simeq 0.5$)[6] with no cluster formation .

The brown - form chelates exhibited the same covalency trends as the green ones with inconsistencies in these trends as calculated from variations of $g_{\parallel}$ and $A_{\parallel}$. Table (3) shows the covalency of complexes under investigation. Such a behaviour was explained previously[1] as due to a continuously changing fraction of the metal 4s character in the $| d_{x^2 - y^2} \rangle$ ground state .

Author would like to thank Dr. M.Isskander , Alexandria University for prepearing the complexes.

REFERENCES :

1. Hedewy.S , Issa M.A , Isskander.M, Spect. Letters 11,11(1978), 1
2. Altshuler. SA, Kozyrew. BM, Electron paramagnetic resonance, Translation editor,CP Poole (Jr)(Academic Press, Inc.,New York), 1964
3. Prew , Swarup , Can. J. Physics, 37 (1959), 484
4. Poole (Jr) cp, Electron spin resonance (Interscience Publishers, Inc., New York), 1967
5. Bleany.B, Bowers . KD , Trenam. RS, Proc. R. Soc. A 228(1955), 157
6. Fujiwara.S, Katsumata,S , Seki.T , J.Phys.Chem. 71,1(1967),115

Received 3-29-79
Accepted 4-04-79