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Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt19

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Aryldecahydroquinolin-4onedithiocarbamato)metal(II) Complexes: A New Preparative Method and Characterization Along with ¹³C and ¹H NMR Decoupling Studies

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To cite this article: V. Venkatachalam, K. Ramalingam, D. Natarajan & N. Bhavani (1996) bis(2-Aryldecahydroquinolin-4-onedithiocarbamato)-metal(II)

Complexes: A New Preparative Method and Characterization Along with $^{\rm 13}{\rm C}$ and

¹H NMR Decoupling Studies, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 26:5, 735-759, DOI: <u>10.1080/00945719608004332</u>

To link to this article: <u>http://dx.doi.org/10.1080/00945719608004332</u>

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BIS(2-ARYLDECAHYDROQUINOLIN-4-ONEDITHIOCARBAMATO)-METAL(II) COMPLEXES: A NEW PREPARATIVE METHOD AND CHARACTERIZATION ALONG WITH ¹³C AND ¹H NMR DECOUPLING STUDIES

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ABSTRACT

2-Aryldecahydroquinolin-4-ones, unlike mere piperidines, do not form dithiocarbamic acids on addition of carbon disulphide under alkaline condition. Invariably, xanthates are formed when carbon disulphide is added to the amine in the presence of alcohol. In the present study dithiocarbamato complexes involving 2-aryldecahydroquinolin-4-ones and Ni(II) and Cu(II) metal ions are reported for the first time. The deprotonation of 2-aryldecahydroquinolin-4-ones takes place in a NH₃/NH₄Cl buffer medium (pH=10) in acetonitrile followed by the addition of carbon disulphide and the corresponding aqueous solution of the metal ion. The isolated complexes were of the formula M(Ldtc)₂; M(II) = Ni(II) and Cu(II),

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Ldtc⁻ = 2-aryldecahydroquinolin-4-onedithiocarbamate anion derivatives. These complexes were characterized by microanalyses, IR, UV, TG and mass spectral studies. A representative nickcl(II) complex has also been subjected to an extensive ¹H NMR decoupling study along with ¹³C NMR and mass spectral analysis, clearly indicating the manifestation of complexation on the stereochemistry of the bicyclic ring of the ligand frame work. ¹H NMR spectral data indicated the significance of the 'thioureide' structure contribution to the stability of the present set of complexes which is not available from IR studies. The downfield shift of the ¹H NMR signals and the upfield shift of the C(2) carbon in ¹³C NMR spectra of the complexes indicates that the heterocyclic ring deviates from the normal chair conformation on complexation.

INTRODUCTION

Nucleophilic attack of carbon disulphide on secondary amines to give rise to stable dithiocarbamic acid ligands has been studied extensively¹. These ligands form stable complexes with transition metal ions. There is a great deal of interest associated with their geometry and reactivity, apart from their use as analytical reagents, vulcanizers, fungicides and pesticides¹. The transition metal ions readily form complexes with different dithiocarbamates which show interesting reactivity patterns². In the present study, a routine attempt to convert different 2-aryl-3-alkyldecahydroquinolin-4-ones in alcohol to the corresponding dithiocarbamic acid ligands was made. The decahydroquinolin-4-ones, L¹ to L⁵, employed in the present study are the following:



Ar



L^1	C ₆ H ₅	н	н
L^2	p-CH ₃ C ₆ H ₄	н	Н
L ³	C ₆ H ₅	н	CH ₃
L ⁴	C ₆ H ₅	CH ₃	CH ₃
L ⁵	C H	CH,CH,	CH ₃

Fig. 1. Structure of the Ligand Precursors

Unlike the other heterocyclic amines (piperidine, morpholine), the 2-aryldecahydroquinolin-4-one derivatives in alcohol did not form the dithiocarbamates but only the ethylxanthate was formed. A modified approach was used to deprotonate the N-H proton of the 2-aryldecahydroquinolin-4-one. Deprotonation takes place only at a higher pH in a NH₃/NH₄Cl buffer medium (pH=10) in acetonitrile followed by the addition of the corresponding aqueous metal ion solution. The isolated complexes were of the general formula M(Ldtc)2.

EXPERIMENTAL

All the chemicals and solvents used were of analytical grade. ¹H NMR and ¹³C NMR spectra were recorded on a Jeol JNM-GSX 400

 \mathbf{R}^2

MHz FTNMR instrument in CDCl₃ at room temperature. The mass spectra were recorded with a HP-4988A apparatus, working in the injection direct probe mode, with a heating ramp of 25-700°C at a heating rate of 40°C/min. Infrared spectra were recorded in the range 4000-400 cm⁻¹ as KBr discs on a JASCO IR-700 infrared spectrophotometer. Electronic spectra were recorded on a JASCO UVIDEC - 650 double beam spectrophotometer using chloroform as the solvent. Thermograms were recorded on a Stanton Redcraft thermobalance with a heating rate of 20°C per minute. Elemental analyses were carried out with an Heraeus Carlo Erba 1108 instrument.

Preparation of Ligands (2 - aryldecahydroquinolin - 4 - ones)

2-Aryldacehydroquinolin-4-ones have been prepared as described earlier^{3,4}.

Preparation of Ni(II) and Cu(II) Complexes

A quantity of 0.45 g (2 mmol) of 2-aryldecahydroquinolin-4-one (L^1) was dissolved in 50 mL of acetonitrile and 2 mL of NH_3/NH_4Cl buffer solution (pH=10) was added followed by 2 mL of carbon disulphide with constant stirring to give the corresponding yellow coloured dithiocarbamic acid. Attempts to separate the free dithiocarbamic acid ligand of the 2-aryldecahydroquinolin-4-ones L^1 to L^5 were unsuccessful. Therefore, the ligands were prepared fresh everytime. An aqueous solution of metal chloride (1 mmol, 0.25 g) was added to the above ligand solution dropwise with continuous stirring. Green coloured dithiocarbamato complexes separated out. The solids were filtered and washed with water, alcohol and

finally with ether and subsequently dried over anhydrous calcium chloride. The same procedure was employed for the preparations of the other 2-aryldecahydroquinolin-4-one (viz. L^2 to L^5) complexes. Analytical and spectral data of the synthesized dithiocarbamato complexes are presented in Tables I and II, respectively.

RESULTS AND DISCUSSION

Synthesis

The following equations show the general method of preparation of the complexes

$$L \qquad \frac{CH_{3}CN/NH_{3}-NH_{4}Cl}{CS_{2}} > Ldtc^{-1}$$
(1)

$$MCl_2 + 2Ldtc' \xrightarrow{CH_3CN} M(Ldtc)_2$$
 (2)

Ldtc' = 2-Aryldecahydroquinoline-4-onedithiocarbamate anion derivatives; M = Ni(II) and Cu(II)

Infrared Spectra

Infrared spectroscopy has proved to be a valuable tool in the study of the stereochemistry of heterocyclic compounds, mainly on the basis of a series of bands in the region 2800 - 2600 cm⁻¹ called Bohlmann bands⁵. These bands have also been used in the assessment of conformational equilibria in decahydroquinolines⁵. Also in the present case the Bohlmann bands of the parent amines appear in the region of 2800 - 2600 cm⁻¹. These

Table I.Analytical and Spectral Data of Bis(2-aryldecahydroquinolin-4-
onedithiocarbamato)M(II) Complexes (M = Ni(II) or Cu(II)).

Complexes	Empirical	H.wt	x	C		хн		XN	x	H	VC-N	\ C-S
:	TOTINULS		Expt	Theo	Expt	Theo	Expt	Theo	Expt	Theo	(infoureice) -1 cm	ся-1
Ní(L ¹ dtc) ₂	C_H_N_O_S_NI 32 38 2 2 4	669.3	56.6	57.4	5.3	5.6	4.2	4.2	8.4	8.8	1424	1012
Ni(L ² dtc) ₂	C H N O S Ni 34 40 2 2 4	695.3	57.6	58.7	5.7	5.7	4.0	4.0	8.0	8.4	1426	1013
Ni(L ³ dtc) ₂	C H N O S N I 34 40 2 2 4	695.3	58.8	58.7	5.8	5.8	4.0	4.0	8.1	8.4	1427	1026
Ni(L ⁴ dtc) ₂	C_H_N_O_S_N1	723.3	58.6	59.7	6.1	6.1	3.9	3.9	7.6	8.1	1423	1020
Ni(L ⁵ dtc) ₂	C_H_N_D_S_Ni 364442254Ni	723.3	59.2	59.7	6.1	6.1	3.5	3.9	7.9	8.1	1423	1015
Cu(L ¹ dte) ₂	C H N O S C U	674.1	56.5	57.0	5.0	5.6	4.0	4.1	9.0	9.4	1412	1015
Cu(L ² dtc) ₂	C_H_N_O_S_CU	700.1	57.8	58.3	5.3	5.7	3.6	4.0	8.6	9.0	1412	1012
Cu(L ³ dtc) ₂	C_H_N_O_S_CU	700.1	58.0	58.3	5.2	5.7	3.7	4.0	8.4	9.0	1415	1028
Cu(L ⁵ dtc) ₂	C_H_44 Z Z S4CU	728.1	53.9	54.6	5.0	5.6	3.2	3.8	8.2	8.7	1414	1013

Expt = Experimental Value Theo = Theoretical Value

bands disappear on complexation due to the lack of antiperiplanarity with respect to the lone pair of electrons as a result of the change in conformation. The carbonyl $\vee C=O$ vibrations appear around 1717 cm⁻¹ in the parent amines and show a shift to higher wave number by 20 cm⁻¹ on complexation. This shift is probably due to some conformational changes which occur on complexation. Because of the fact that the dithiocarbamate complexes are confirmed to be containing the MS₄ chromophore, the probability for Table II. ¹H NMR Spectral Data of Ni(Ldtc)₂ Complexes and the Corresponding Parent Amines (ppm).

Complexes	N-H in the parent amine	с(2)-н	С(3)-Н	с(9)-Н	с(10)-Н	с(5)-с(8)н	с(3)-сн ₃	c(3)-cH ₂	Aromatic Protons
Ni(Letc),		6.40	3.38,2,87	3.97	2.35	2.90-0.90	1	1	7.30-7.23
- - -	1.60	4.02	2.60,2.53	2.63	2.19	2.02-1.22	ł	1	7.41-7.26
Ni(L ³ dtc),		6.15	3.38	3.92	2.95	1.61-0.81	1.34	ł	7.45-7.24
г ₃	1.67	3.53	2.65	2.65	2.28	1.98-1.19	0.76	I	7.39-7.26
Ni(L ⁴ dtc) ₂		6.05	1	3.90	2.69	2.80-0.50	1.48,1.60	I	7.45-7.20
1.4 1	1.63	3.71	I	2.54	2.48	2.17-1.16	0.90,1.10	1	7.44-7.24
Ni(L ⁵ dtc) ₂		6.25	3.12	3.86	2.30	2.06-0.98	1.18	1.18	7.48-7.24
г. г	1.63	3.63	2.56	2.56	2.28	1.95-1.00	0.72	1.59,1.04	7.40-7.26

carbonyl group coordination is remote and the shift in vC=0 on complexation may be attributed to conformational changes of the decahydroquinolines.

In the present set of complexes vC-N vibrations occur around 1420 cm⁻¹. It is observed that the vC-N mode of the heterocyclic dithiocarbamates occurs at lower wave numbers than the vC-N band of the dialkyldithiocarbamates. This is because the contribution of the polar thioureide structure is significant for the dialkyldithiocarbamato complexes and less significant for the heterocyclic dithiocarbamates⁶. The lower vC-N values indicate that the rigid heterocyclic ring systems show less tendency to delocalize electrons between the carbon-nitrogen bonds⁷. In the present study, the occurrence of a single vC-S band at 1017 cm⁻¹ in all the dithiocarbamato complexes indicates the uninegative bidentate behaviour of all the dithiocarbamate ligands⁸.

Electronic Spectra

The electronic spectra of the Ni(II) and Cu(II) complexes were recorded in chloroform. In all the Ni(II) complexes, bands which appear below 350 nm are due to the intraligand $\pi \rightarrow \pi^*$ charge transfer transitions mainly associated with N-C=S and S-C=S groups, while the band at 374 nm is due to the $n \rightarrow \pi^*$ transition⁹. Several authors ascribe intense bands in the 404-458 nm region to either metal \rightarrow ligand or ligand \rightarrow metal charge transfer processes¹⁰. In addition to these charge transfer bands, the electronic spectra show a hump at 490 nm and a broad band at 637 nm which are due to the d-d transitions¹¹. In the case of dialkyldithiocarbamato complexes of nickel(II), similar bands were reported and these were ascribed to transitions from the lower filled **d** orbitals to the unoccupied dx^2-y^2 orbital¹². The two bands at 637 nm and 490 nm correspond to the $dxy \rightarrow dx^2-y^2$ and $dz^2 \rightarrow dx^2-y^2$ transitions. The positions corresponding to the $dxz \rightarrow dx^2-y^2$ and $dyz \rightarrow dx^2-y^2$ transitions would be between the $dxy \rightarrow dx^2-y^2$ (637 nm) and $dz^2 \rightarrow dx^2-y^2$ (490 nm) transitions. Of the two transitions, one is observed at 564 nm due to the $dxz \rightarrow dx^2-y^2$ transition and the other is lost in the broadening of the 637 nm band. However, Dingle¹³, by using single crystals and polarized light, suggested the existence of two bands at 588 and 526 nm from the $dxz \rightarrow dx^2-y^2$ and $dyz \rightarrow dx^2-y^2$ transitions for bis(dialkyldithiocarbamato)nickel(II) complexes. All the Ni(II) complexes are diamagnetic, as expected for low spin d⁸ complexes, and hence should be of square-planar geometry¹⁴.

In the case of Cu(II) complexes the band at 441 nm corresponds to charge transfer transitions¹⁵ and the bands at 520 and 640 nm are assigned to the d-d transitions of the Cu(II) ion, indicative of a square-planar geometry around the metal ion. The Cu(II) complexes had a magnetic moment equivalent to 1.8 BM.

¹H NMR Spectra

¹H NMR spectra of bis(2-aryl-3-alkyldecahydroquinolin-4onedithiocarbamato)nickel(II) complexes were recorded in CDCl₃ at ambient temperature and the chemical shift values are presented in Table II along with the chemical shift values of the parent decahydroquinolines for comparison. It is interesting to note that, the ¹H NMR signals of the various protons are well separated after complexation, as expected. This then made the job of identifying the individual signals corresponding to different protons by decoupling experiments easier. Figs. 2 and 3 are the ¹H NMR and ¹³C NMR spectra of the bis(2-phenyl-3-methyldecahydroquinolin-4-onedithiocarbamato)nickel(II) complex.

The downfield shift of the C(2) and C(9) protons in all the complexes is probably an indication of the important consequence of the complexation process viz., a significant thioureide $N^{\delta+}C^{\delta-}$ contribution to the stability of the complexes and a resultant reduction in the electron density in its vicinity. The downfield shift is more pronounced in the case of the C(2) proton compared to the C(9) proton, probably because of the conformational changes associated with the complexation and hence the 'pitch' of the phenyl ring also varies.

The formation of the dithiocarbamato complexes is confirmed by the absence of the >N-H proton signal, which appears around 1.60 ppm in the parent amines¹⁶. In all the dithicarbamato complexes and the corresponding parent amines, the aromatic proton signals appear in the region around 7 ppm. The alkyl proton signals at C(3) in the complexes L³-L⁵ appear in the region 1.60 - 1.20 ppm. These alkyl protons shield the benzylic protons at C(2) significantly and the shielding effect is in the order of methyl > ethyl > dimethyl as observed in the parent amines¹⁶. The carbocyclic C(5), C(6), C(7) and C(8) ring proton signals appear in the upfield region at 0.90 - 2.80 ppm and there is not a considerable shift in these protons when compared with those of the parent amines.

In all the dithiocarbamato complexes the benzylic proton signals at C(2) appear around 6 ppm, which indicates deshielding by approximately 2 ppm, when compared with the parent amines. The downfield shift is







probably due to the partial involvement of the pair of electrons of the N-C(2) bond, due to the delocalization of the lone pair of electrons on the nitrogen in the thioureide bond. The two ring junction proton signals of the complexes at C(9) and C(10) appear around 3.90 and 2.30 ppm, respectively. Of the two ring junction protons, C(9) is more deshielded than the other, due to the presence of a hetero atom adjacent to it. In the complexes Ni(L¹dtc)₂ and Ni(L²dtc)₂ the methylene protons at C(3) appear around 3.38 and 2.87 ppm, respectively. This is due to the axial and equatorial protons at C(3), whereas in the 3-alkyl complexes an unresolved multiplet appears at 3 ppm.

Decoupling Experiments

The above assignment of the signals were confirmed by decoupling experiments¹⁷. Figs. 4 and 5 depict the decoupled ¹H NMR spectra for irradiation of some of the protons to identify the various signals. The eight different spectra, a to h describe following proton irradiations and the corresponding decouplings (a). Irradiation of C(9)-H decouples C(8)-H and C(10)-H, (b). Irradiation of C(10)-H decouples C(9)-H (C(5)-H decoupling is obscured by the multiplet), (c). Irradiation of C(3)-H decouples C(3)-CH₂, (d). Irradiation of C(3)-CH₃ decouples C(3)-H, (e). Irradiation of C(8)-H decouples C(7)-H and C(9)-H, (f). Irradiation of C(7)-H decouples C(6)-H and C(8)-H, (g). Irradiation of C(6)-H decouples C(7)-H, (h). Irradiation of C(7)-H (equitorial) decouples C(8)-H. The equitorial and axial proton signals of the cyclohexyl ring carbons, C(5) to C(8) appear well separated. Only one of the signal decoupling is shown in the figures. The decoupling experiments carried out in the present study are summarized in Fig. 6. A vertical arrow points to the irradiated signal, whilst vertical lines point to the signals which were simplified by the loss of coupling.



Fig. 4. Proton Decoupled Spectra of Bis(2-phenyl-3-methyldecahydroquinolin-4onedithiocarbamato)Ni(II) Complex. (a to d are explained in the text)



Figure 4. Continued



Fig. 5. Proton Decoupled Spectra of Bis(2-phenyl-3-methyldecahydroquinolin-4onedithiocarbamato)Ni(II) Complex. (e to h are explained in the text)



Figure 5. Continued



Fig. 6. Summary of Decoupling Experiments^a

a = Vertical arrow: irradiated signal; vertical line: observed (affected or decoupled) signal

Decoupling of the benzylic protons at C(2) affects the methine proton signal at C(3) which indicates the coupling between C(2) and C(3) protons. Irradiation of the C(9) proton decouples the C(8) and C(10) protons and C(10) proton irradiation decouples the C(5) and C(9) protons. This shows that C(9) and C(10) are the ring junction protons. On irradiation of the 3-alkyl protons, the methine proton signals are decoupled indicating the coupling between these protons. Irradiation of the carbocyclic ring methylene protons at C(5) and C(8) decoupled the signals of the C(6), C(10) protons and C(7) and C(9) protons, respectively. This shows that the C(5) and C(8) protons are the neighbouring protons to the ring junction protons. The C(7) proton decoupling showed coupling between C(6), C(7) and C(8) protons. The entire sequence of double resonance experiment on the complex identified all the proton signals without any ambiguity.

The observed signals in the ¹H NMR spectra of all the dithiocarbamato complexes are deshielded when compared with the corresponding proton signals of the parent decahydroquinolin-4-ones. The deshielding effect is greater for those protons situated near the central metal ion and less pronounced for distant protons¹⁸. The downfield shift of proton signals in all the dithiocarbamato complexes supports the bidentate nature of the dithiocarbamate ligand¹⁹. In the case of bidentate coordination involving the dithiocarbamate ligands, the deshielding of protons is due to the drift of electron density from nitrogen towards carbon leading to a larger contribution of thioureide form to the structure²⁰.

¹³C NMR Spectra

In addition to the ¹H NMR studies 13 C NMR spectra were recorded for the Ni(L³dtc)₂ complex (CDCl₃ as solvent) at room temperature to support the proposed structural formula. The spectrum shows signals at 15.5, 24.2, 24.3, 24.8, 32.6, 44.2, 49.3, 60.8, 61.6, 76.1, 76.5, 76.7, 77.0, 125.8, 127.8 and 137.2 ppm.

The carbocyclic ring carbon C(5), C(6), C(7) and C(8) signals appear at 24.2, 24.3, 24.8 and 32.6 ppm whereas in the case of the parent decahydroquinolin-4-one these signals appear around 26 and 33.9 ppm, respectively, which indicates that there is no significant change in the carbocyclic ring conformation.

The heterocyclic ring carbon signals for C(2) and C(9) adjacent to the hetero atom appear at 61.6 and 60.8 ppm but these two signals appear at 69.2 and 62.1 ppm in the corresponding parent decahydroquinolin-4-one. The remaining signals at 49.3, 44.2 and 15.5 ppm are assigned to C(10), C(3) and methyl carbon atoms.

The phenyl ring carbon signals appear in the downfield region at 125.8, 127.8, 128.7 and 137.2 ppm. Among these four, the signal at 137.2 ppm is ascribed to the *ipso*-carbon atom of the phenyl ring²¹. The carbonyl and the NCS₂ carbon signals in most of the dialkyldithiocarbamato complexes appear around 200 ppm²². The downfield shift of the ¹H NMR signals and the upfield shift of the C(2) carbon in the ¹³C NMR spectra of the complexes indicates that the heterocyclic ring deviates from the normal chair conformation on complexation.¹⁶

Thermogravimetric Studies

The temperature range and percentage weight losses of the decomposition reactions are given in the Table III. The TG curves obtained for all the complexes are similar, showing a single stage weight loss, which corresponds to the formation of metal thiocyanate as an intermediate and which may yield ultimately the metal sulphide. Most of the thermal decomposition studies of dithiocarbamato complexes show that the formation of the corresponding metal thiocyanate is an essential step²³.

DITHIOCARBAMATO METAL(II) COMPLEXES

Complexes	Initial decomp. Temp.°C	Decomposi -tion Temp.°C	Fraction remaining at the end of the first step decomp.	Final experimental residue	Composition of the final residue
Ni(L ¹ dtc) ₂	335	335-360	0.20	0.03	Nis ^a
Ni(L ² dtc) ₂	345	345-365	0.53	0.28	NiS+Ni(SCN) ₂
Ni(L ³ dtc) ₂	346	346-385	0.45	0.36	NiS+Ni(SCN)2
NI(L ⁴ dtc) ₂	370	370-400	0.29	0.15	NiSO4
Ni(L ⁵ dtc) ₂	350	350-385	0.37	0.26	NiS+Ni(SCN)2
Cu(L ¹ dtc) ₂	300	300-360	0.46	0.39	Cu(SCN)2+CuS
Cu(L ² dtc) ₂	300	300-350	0.48	0.30	Cu(SCN)2+CuS
Cu(L ³ dtc) ₂	250	250-360	0.42	0.33	Cu(SCN)2+CuS
Cu(L ⁵ dtc) ₂	315	315-360	0.34	0.32	Cu(SCN)2+CuS
1	1		1	1	1

Table III.	Thermogravimetric Analyses of M(Ldtc) ₂ Complexes
	(M = Ni(II) or Cu(II)).

a Final temperature is > 550°C

b Final temperature is > 600°C

Thermograms of all the complexes show an initial decomposition around 250°C which indicates the absence of solvent molecules. In the case of the Ni(II) complexes, the initial decomposition is in the range 325 - 370°C followed by a rapid weight loss (a minimum of 60%) and ends around 400°C. It indicates the pyrolysis of the organic moiety, as shown by the intense DTA peaks²⁴. The residue obtained at this temperature did not agree stoichiometrically with simple binary salts of the metal. Ultimately, the final residues obtained in the thermograms agreed well with the calculated weights of a 1:1 mixture of Ni(SCN)₂ and NiS²⁵. It is also interesting to note that at still higher temperature NiS is converted to NiSO₄.

The thermal decomposition of the Cu(II) complexes commences in the range 250-315°C followed by a weight loss to the extent of 60%. In all of the Cu(II) complexes a sharp endothermic peak appears prior to the pyrolysis of the carbonaceous material which may due to a phase change. The exothermic peaks present in the temperature range 250-360°C are due to the pyrolysis of the organic moiety attached to the metal ion²⁴. As observed in the case of the nickel(II) complexes, the fast pyrolysis process does not give rise to Cu(SCN)₂ or CuS directly, but these are formed ultimately after the loss of probably a little more carbonaceous material attached to them. A comparison of the thermograms of the Ni(II) and Cu(II) complexes show that the former are more stable than the latter. All the end point products were identified by X-ray powder patterns. The thermal analyses of the complexes confirm the proposed molecular formulae of the complexes.

Mass Spectra

The mass spectrum of the Ni $(L^3 dtc)_2$ complex shows the molecular ion peak of m/e = 694 with the high relative intensity of 100% which supports the proposed molecular weight as well as molecular formula of the complexes. The medium intensity peak at m/e = 174 is assigned to the Ni(SCN)₂ fragment supported by the TG analysis as an intermediate product during the pyrolysis process of the complex.

CONCLUSIONS

Five 2-aryldecahydroquinolin-4-ones form bis(dithiocarbamato)M(II) complexes (where M = Ni(II) and Cu(II)) at pH=10 in acetonitrile water solution.



Fig. 7. Schematic Representation of the Complexes

The analyses of the complexes confirm the general formula M(Ldtc)₂. The stoichiometry was also confirmed by TG analyses; the nickel complexes were found to be more stable than their copper analogues with respect to pyrolysis. The end products of the thermal analyses were found invariably to be a mixture of M(SCN), Infrared studies of the complexes indicated the bidentate mode of the + MS. dithiocarbamate ligand. Also, the contribution of the thioureide structure is moderate as is indicated by the C-N frequencies for the complexes which lie at around 1425 cm⁻¹ for the nickel complexes and around 1413 cm⁻¹ for the copper analogues. However, a detailed ¹H NMR study of the complexes, including decoupling experiments, identified the signals due to individual protons and the significance of the thioureide contribution to the structure. A more pronounced downfield shift of the C(2) proton supports the significance of the 'thioureide' contribution, in addition to the effects of conformational changes, upon complexation. The downfield shift of the ¹H NMR signals and the upfield shift of the C(2) carbon signal in the ¹³C NMR spectra of the complexes indicates that the heterocyclic ring deviates from the normal chair conformation found in the N-substituted decahydroquinolines. However, the

carbocyclic ring is the least affected on complexation. The schematic representation of the complexes is shown in Fig. 7.

The electronic spectral and magnetic moment data indicate the planarity of the MS_4 chromophore. Though the complexes are highly soluble in chloroform, efforts to crystallize them to have a better understanding on the structure have not been successful sofar. But efforts are continued to obtain suitable crystals for a single crystal X-ray structure determination.

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Received:	21 February 1995	Referee I:	J. L. Walsh
Accepted:	16 January 1996	Referee II:	K. Moedritzer

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