This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Studies on Polymeric Base Derivatives of Some Copper(II) Orthohydroxy Thiosemicarbazones

L. D. Dave[a]; Pankras Francis[a]; S. K. Thampy[b]
[a] Department of Chemistry, Bhavnagar University, Bhavnagar, India [b] C.S.M.C.R.I., Bhavnagar, India

To cite this Article Dave, L. D. , Francis, Pankras and Thampy, S. K.(1983) 'Studies on Polymeric Base Derivatives of Some Copper(II) Orthohydroxy Thiosemicarbazones', Journal of Macromolecular Science, Part A, 20: 3, 365 — 376
To link to this Article: DOI: 10.1080/00222338308063286
URL: http://dx.doi.org/10.1080/00222338308063286

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. MACROMOL. SCI.–CHEM., A20(3), pp. 365-376 (1983)

Studies on Polymeric Base Derivatives of Some Copper(II) Orthohydroxy Thiosemicarbazones

L. D. DAVE and PANKRAS FRANCIS

Department of Chemistry
Bhavnagar University
Bhavnagar 364002, India

S. K. THAMPY

C.S.M.C.R.I.
Bhavnagar 364002, India

Downloaded At: 19:58 24 January 2011

ABSTRACT

Polymeric complexes of copper(II) with some orthohydroxy thiosemicarbazones (H_2L), such as 2-OH-5-Me (Cl), aceto/propiophenone thiosemicarbazones with some bases (B), viz., pyridine; α-, β-, γ-picolines; piperidine; morpholine and bidentate bases; bipy and o-phen, have been isolated and characterized. The analytical data shows them to have 1:1:1 composition of Cu:L:B. Their thermal, spectral, and magnetic properties are studied.

INTRODUCTION

Aromatic thiosemicarbazones having an –OH group in the ortho position have been studied for complex formation [1]. Some of the derivatives of thiosemicarbazones have also attracted special attention due to their anticancer, antibacterial, antifungal, and antitubercular activities [2, 3]. Here we report some base adducts of polychelates of copper(II) ions formed by the condensation of four o-

Copyright © 1983 by Marcel Dekker, Inc.

0022-233X/83/2003-0365$3.50/0

hydroxy ketones with thiosemicarbazides along with their physicochemical properties. The metal complexes of dibasic tridentate ligands assume a variety of stereochemical forms [4] depending upon the nature of the metal ion used. The stereochemistry of polymers is studied here using data from electronic, infrared, and ESR spectra as well as from magnetic susceptibility, conductivity, and thermal analysis.

EXPERIMENTAL

Material

All the materials used were of A.R. quality.

The ligands were prepared by refluxing four ketones, viz., 2-OH-5-Me/Cl aceto- and propiophenones, with thiosemicarbazide for about 3 h. The mixture was poured on ice and the solid which separated was crystallized from alcohol. The base adducts were prepared by refluxing the metal chelates with the respective base and then pumping out the excess base in vacuum. For the preparation of bidentate base (bipy and o-phen) adducts, the bases were refluxed with the metal complex in chloroform. All the adducts were found to be insoluble in common organic solvents. The slight solubility of all these complexes in chloroform was enough for ESR work, though not large enough for ebulloscopic determination of molecular weight. The complexes were found to be soluble in DMF and DMSO and were quite stable at room temperature.

Downloaded At: 19:58 24 January 2011

Measurements

The magnetic susceptibility of the solids was determined at room temperature by the Gouy method. Electronic spectrum was measured on a Spectronic-20. IR spectra were recorded on a Spectromom-2000 spectrometer in the range 4000-700 cm^{-1} and on a Fourier Far IR spectrometer in the range 600-100 cm^{-1}. The ESR spectra were measured on a Varian E_4, DPR spectrometer operating at ~9.0 to 9.4 GHz and 100 kHz field modulation and phase sensitive detections. The conductivity was measured on a Toshniwal conductivity bridge. The thermal analyses were performed in a TGA analyser model TGA-2TR supplied by M/s. Laboratories, Calcutta, and DTA using a recording DTA Steuerteil, Veb Laboralasktronik.

RESULTS AND DISCUSSION

The elemental analyses (Table 1) done by standard methods show that the complexes exhibit 1:1:1 stoichiometry of metal:ligand:base.

Downloaded At: 19:58 24 January 2011

TABLE 1. Analytical Data of Copper(II) Complexes

No.	Name of chelate[a]	C (%)	H (%)	N (%)	S (%)	Cu (%)	eff (B.M.)
1	2-OH-5-Me acetophenone tsc Cu(II)py	49.50 (49.57)	4.35 (4.40)	15.32 (15.4)	8.72 (8.80)	17.42 (17.47)	1.76
2	2-OH-5-Me propiophenone tsc Cu(II)py	50.65 (50.58)	4.74 (4.70)	14.65 (14.83)	8.35 (8.47)	16.85 (16.83)	1.73
3	2-OH-5-Cl acetophenone tsc Cu(II)py	43.52 (43.74)	3.45 (3.38)	14.40 (14.58)	8.15 (8.33)	16.45 (16.54)	1.8
4	2-OH-5-Cl propiophenone tsc Cu(II)py	45.38 (45.22)	3.71 (3.76)	13.95 (14.06)	7.90 (8.04)	15.75 (15.96)	1.77
5	2-OH-5-Me acetophenone tsc Cu(II)α-pic	50.91 (50.8)	4.46 (4.76)	14.80 (14.88)	8.37 (8.5)	16.60 (16.8)	1.74
6	2-OH-5-Me propiophenone tsc Cu(II)α-pic	52.4 (52.1)	5.02 (5.1)	14.43 (14.3)	8.25 (8.2)	15.96 (16.2)	1.71
7	2-OH-5-Cl acetophenone tsc Cu(II)α-pic	45.03 (45.2)	3.86 (3.76)	13.95 (14.1)	7.76 (8.03)	15.75 (15.95)	1.72
8	2-OH-5-Cl propiophenone tsc Cu(II)α-pic	46.72 (46.6)	3.91 (4.1)	13.68 (13.59)	7.52 (7.76)	15.3 (15.4)	1.8
9	2-OH-5-Me acetophenone tsc Cu(II)β-pic	50.65 (50.8)	4.81 (4.76)	14.5 (14.8)	8.36 (8.5)	16.68 (16.8)	1.74
10	2-OH-5-Me propiophenone	51.98 (52.1)	5.04 (5.1)	14.46 (14.3)	7.96 (8.2)	16.02 (16.2)	1.73

(continued)

Downloaded At: 19:58 24 January 2011

TABLE 1 (continued)

No.	Name of chelate[a]	C (%)	H (%)	N (%)	S (%)	Cu (%)	eff (B.M.)
11	2-OH-5-Cl acetophenone tsc Cu(II)β-pic	44.95 (45.2)	3.81 (3.76)	13.73 (14.1)	8.01 (8.03)	15.6 (15.9)	1.73
12	2-OH-5-Cl propiophenone tsc Cu(II)β-pic	46.74 (46.6)	3.91 (4.1)	13.45 (13.59)	7.55 (7.7)	15.32 (15.4)	1.70
13	2-OH-5-Me acetophenone tsc Cu(II)γ-pic	50.5 (50.8)	4.82 (4.76)	14.58 (14.8)	8.43 (8.5)	16.57 (16.8)	1.76
14	2-OH-5-Me propiophenone tsc Cu(II)γ-pic	52.24 (52.1)	5.01 (5.1)	14.45 (14.3)	8.1 (8.2)	15.93 (16.2)	1.74
15	2-OH-5-Cl acetophenone tsc Cu(II)γ-pic	44.93 (45.2)	3.66 (3.76)	13.8 (14.1)	7.8 (8.03)	15.84 (15.95)	1.72
16	2-OH-5-Cl propiophenone tsc Cu(II)γ-pic	46.4 (46.6)	3.77 (4.1)	13.71 (13.6)	7.72 (7.76)	15.33 (15.41)	1.68
17	2-OH-5-Me acetophenone tsc Cu(II)pip	48.63 (48.71)	5.98 (5.95)	15.06 (15.15)	8.57 (8.68)	17.03 (17.18)	1.71
18	2-OH-5-Me propiophenone tsc Cu(II)pip	50.33 (50.06)	6.04 (6.25)	14.73 (14.60)	8.11 (8.34)	16.54 (16.55)	1.75
19	2-OH-5-Cl acetophenone tsc Cu(II)pip	43.24 (43.07)	4.89 (4.87)	14.46 (14.35)	7.96 (8.02)	16.22 (16.29)	1.8
20	2-OH-5-Cl propiophenone tsc Cu(II)pip	44.81 (44.79)	5.36 (5.19)	13.82 (13.86)	7.77 (7.92)	15.75 (15.73)	1.74
21	2-OH-5-Me acetophenone tsc Cu(II)mor	45.42 (45.22)	5.25 (5.38)	15.10 (15.07)	8.58 (8.60)	17.02 (17.09)	1.70

Downloaded At: 19:58 24 January 2011

22	2-OH-5-Me propiophenone tsc Cu(II)mor	46.78 (46.69)	5.66 (5.70)	14.66 (14.52)	8.02 (8.30)	14.43 (16.47)	1.72
23	2-OH-5-Cl acetophenone tsc Cu(II)mor	40.14 (39.79)	4.42 (4.30)	13.91 (14.28)	8.04 (8.16)	16.17 (16.20)	1.80
24	2-OH-5-Cl propiophenone tsc Cu(II)mor	41.17 (41.37)	4.42 (4.67)	13.57 (13.79)	7.74 (7.88)	15.47 (15.64)	1.73
25	2-OH-5-Me acetophenone tsc Cu(II)bipy	54.34 (54.20)	4.85 (4.74)	15.87 (15.80)	6.95 (7.20)	14.31 (14.35)	1.74
26	2-OH-5-Me propiophenone tsc Cu(II)bipy	54.93 (55.19)	4.71 (5.03)	15.24 (15.30)	6.92 (7.00)	13.77 (13.90)	1.73
27	2-OH-5-Cl acetophenone tsc Cu(II)bipy	49.04 (49.2)	3.54 (3.88)	14.73 (15.10)	6.82 (6.90)	13.64 (13.70)	1.71
28	2-OH-5-Cl propiophenone tsc Cu(II)bipy	50.54 (50.30)	3.91 (4.19)	14.71 (14.67)	6.40 (6.70)	13.04 (13.30)	1.75
29	2-OH-5-Me acetophenone tsc Cu(II)o-phen	56.43 (56.80)	4.30 (4.09)	15.20 (15.06)	6.62 (6.88)	13.53 (13.67)	1.80
30	2-OH-5-Me propiophenone tsc Cu(II)o-phen	57.8 (57.67)	4.02 (4.38)	14.71 (14.60)	6.48 (6.68)	13.31 (13.27)	1.74
31	2-OH-5-Cl acetophenone tsc Cu(II)o-phen	51.62 (51.95)	3.40 (3.29)	14.04 (14.40)	6.42 (6.59)	12.80 (13.09)	1.71
32	2-OH-5-Cl propiophenone tsc Cu(II)o-phen	52.77 (52.9)	3.42 (3.60)	14.20 (14.02)	6.20 (6.40)	12.56 (12.73)	1.70

[a]tsc = thiosemicarbazone, py = pyridine, pic = picoline, pip = piperidine, mor = morpholine, bipy = bipyridyl, o-phen = o-phenathroline.

The low conductivity (~10 mhos) of all the complexes, measured in DMF, confirms their nonelectrolytic nature.

The DTA curves show an endothermic peak between 210-240°C in all the complexes which we assign to loss of the base molecule. All the complexes gave an exothermic peak around 325°C and the smell of SO_2 was given out. In the TGA analysis all the complexes started giving out the smell of SO_2 mixed with smell of the respective base around 300°C. The residue found could be correlated with the expected stoichiometry.

The magnetic moments of the copper(II) complexes measured at room temperature fall in the range 1.68 to 1.8 B.M. (Table 1). The value is close to the spin-only value, some even having a smaller value. Normally, due to spin-orbit coupling, magnetic moments are higher than the spin-only values. The observed values are, therefore, rather low. A remarkable feature of the magnetochemistry of bivalent copper complexes of dibasic tridentate ligands is the frequency with which evidence of magnetic exchange [5-7] is found, frequently of the superexchange type.

The low magnetic moments in copper(II) complexes are usually attributed to spin-spin coupling within a dimer brought about by the bridging [8-11] of monomeric units of paramagnetic centers. Thus the subnormal or almost "spin-only" magnetic moments observed for the present copper(II) complexes may be accounted for by assuming a polymeric structure in the solid state. Such polymerization could occur through the N, O, or S atom of neighbors. Bulk magnetic susceptibility cannot assist in deciding in favor of either a square planar or a tetragonal arrangement. Both symmetries would be D_{4h} on an idealized representation. However, ESR spectra of these complexes show antiferromagnetic coupling between two copper(II) ions. As this is not reflected in the magnetic moment determined on solids, it is probably a case of weak antiferromagnetic coupling. A low temperature study of magnetic susceptibility could help further.

The electronic spectra of all the adducts show three bands at 19,600, 16,600, and 14,500 cm^{-1}. Copper(II) complexes are subject to considerable distortion which renders their absorption quite complex. The absorption spectra of the copper(II) complexes are not inconsistent with tetragonal geometry for them. The interpretation of these spectra, however, is not easy, as the near neighbors are different and the large value of the spin-orbit coupling causes further splitting of levels, complicating matters to a large extent. Further, the ESR spectra discussed later do point to polymeric species being present in these complexes. A distorted octahedral structure is the most likely structure around copper(II). The three bands would then arise from splitting of levels due to spin-orbit coupling and to different near neighbors round Cu(II) ions. IR spectra of all the complexes show the absence of ν_{OH} but show two ν_{NH_2} bands around 3300 and 3100 cm^{-1}. The $\nu_{(C=N)}$ band is observed at 1610 cm^{-1} with a shoulder, the latter

Downloaded At: 19:58 24 January 2011

probably from the base. We assign the band at ~720 cm^{-1} to $\nu_{(C-S)}$. The low frequency spectrum suggests a clear band at 516-512 cm^{-1} which we assign to $\nu_{(M-N)}$ [12, 13]. Similarly $\nu_{(M-O)}$ could be the band observed at 444-440 cm^{-1}. The band at still lower frequency, i.e., 256 cm^{-1}, has been assigned to $\nu_{(M-S)}$ [14]. This seems to suggest that the chelation takes place through N of the azomethine group, S^- of the mercapto group, and O^- of the phenolic –OH group.

The ESR spectra of the copper(II) complexes are measured and the g-values are given in Table 2. The $g_{\parallel}$ components clearly show seven transitions suggesting three equivalent nitrogens splitting the Cu band. The $g_{\perp}$ band is clearly split giving A_N = 14 G. In all cases, $g_{\parallel} > g_{\perp}$, suggesting that these complexes have axial symmetry. The complexes are considered to be polymeric from the fact that all of them are insoluble or sparingly soluble in common organic solvents. The third nitrogen responsible for this splitting into seven lines could be from a neighboring tsc ligand rather than from the second nitrogen on the ligand already chelated to copper because this would give a strained three-membered ring. Finally, that there are polymeric species present in these complexes seems to be established conclusively by the half-field (~1600 G) spectra at liquid nitrogen temperature which show a weak transition in all the complexes studied. This weak transition obviously is a forbidden one arising from a $\Delta M_s = \pm 2$ transition. This coupling between two copper(II) ions persists in solutions at low temperature, suggesting dimeric species in solution (Fig. 1). The antiferromagnetic exchange coupling between the two copper ions seems to be weak. Such a conclusion seems to be warranted from the bulk magnetic susceptibility data at room temperature which on calculation give magnetic moments not far from the "spin-only" value of 1.73 B.M. Some of these copper(II) complexes have magnetic moments even below 1.73 B.M. Normally magnetic moments around 2.0 B.M. are quite common for copper(II) due to spin-orbit coupling. Lowering of moments is known to occur due to dipolar interaction, Cu(II) acetate monohydrate dimer with a moment of 1.4 B.M. being a famous case. Here, therefore, all these values around 1.7-1.8 B.M. seem to point to a weak exchange between two Cu(II) ions. Further, the G-values [15, 16] are all less than 4, and hence it is concluded that the complexes have weak interaction between copper(II) centers.

ACKNOWLEDGMENT

The authors are thankful to Bhavnager University for a research scholarship to P.F.

Downloaded At: 19:58 24 January 2011

Downloaded At: 19:58 24 January 2011

TABLE 2. ESR Spectral Data on Polycrystalline Copper(II) Complexes

No.	Name of complex[a]	Room temperature			Low temperature		
		$g_{\|}$	$g_{\perp}$	G	$g_{\|}$	$g_{\perp}$	G
1	2-OH-5-Me acetophenone tsc Cu(II)py	2.152	2.052	2.92	2.150	2.054	2.77
2	2-OH-5-Me propiophenone tsc Cu(II)py	2.138	2.061	2.26	2.144	2.047	3.06
3	2-OH-5-Cl acetophenone tsc Cu(II)py	2.143	2.052	2.75	2.168	2.072	2.33
4	2-OH-5-Cl propiophenone tsc Cu(II)py	2.153	2.067	2.28	2.154	2.967	2.30
5	2-OH-5-Me acetophenone tsc Cu(II)α-pic	2.129	2.070	1.80	2.148	2.071	2.08
6	2-OH-5-Me propiophenone tsc Cu(II)α-pic	2.104	2.052	2.00	2.178	2.055	3.20
7	2-OH-5-Cl acetophenone tsc Cu(II)α-pic	2.116	2.054	2.14	2.116	2.054	2.14
8	2-OH-5-Cl propiophenone tsc Cu(II)α-pic	2.167	2.057	2.93	2.182	2.159	3.08
9	2-OH-5-Me acetophenone tsc Cu(II)β-pic	2.142	2.071	2.00	2.153	2.070	2.18
10	2-OH-5-Me propiophenone tsc Cu(II)β-pic	2.135	2.044	3.06	2.146	2.048	3.04

Downloaded At: 19:58 24 January 2011

11	2-OH-5-Cl acetophenone tsc Cu(II)β-pic	2.174	2.068	2.50	2.177	2.069	2.55
12	2-OH-5-Cl propiophenone tsc Cu(II)β-pic	2.160	2.058	2.75	2.162	2.061	2.65
13	2-OH-5-Me acetophenone tsc Cu(II)γ-pic	2.193	2.070	2.75	2.182	2.168	2.67
14	2-OH-5-Me propiophenone tsc Cu(II)γ-pic	2.143	2.047	3.06	2.142	2.047	3.06
15	2-OH-5-Cl acetophenone tsc Cu(II)γ-pic	2.151	2.057	2.60	2.175	2.062	2.82
16	2-OH-5-Cl propiophenone tsc Cu(II)γ-pic	2.119	2.090	2.30	2.183	2.091	2.01
17	2-OH-5-Me acetophenone tsc Cu(II)pip	2.142	2.077	1.84	2.172	2.078	2.20
18	2-OH-5-Me propiophenone tsc Cu(II)pip	2.162	2.081	2.00	2.164	2.081	2.02
19	2-OH-5-Cl acetophenone tsc Cu(II)pip	2.148	2.069	2.01	2.152	2.071	2.01
20	2-OH-5-Cl propiophenone tsc Cu(II)pip	2.172	2.059	3.00	2.174	2.057	3.05
21	2-OH-5-Me acetophenone tsc Cu(II)mor	2.135	2.044	3.06	2.146	2.046	3.20
22	2-OH-5-Me propiophenone tsc Cu(II)mor	2.143	2.053	2.70	2.156	2.054	2.88

(continued)

Downloaded At: 19:58 24 January 2011

TABLE 2 (continued)

No.	Name of complex[a]	Room temperature			Low temperature		
		$g_{\parallel}$	$g_{\perp}$	G	$g_{\parallel}$	$g_{\perp}$	G
23	2-OH-5-Cl acetophenone tsc Cu(II)mor	2.150	2.049	3.06	2.153	2.051	3.00
24	2-OH-5-Cl propiophenone tsc Cu(II)mor	2.174	2.057	3.05	2.174	2.057	3.05
25	2-OH-5-Me acetophenone tsc Cu(II)bipy	2.162	2.061	2.67	2.112	2.041	2.74
26	2-OH-5-Me propiophenone tsc Cu(II)bipy	2.164	2.062	2.64	2.132	2.042	3.14
27	2-OH-5-Cl acetophenone tsc Cu(II)bipy	2.156	2.063	2.47	2.101	2.030	3.30
28	2-OH-5-Cl propiophenone tsc Cu(II)bipy	2.174	2.062	2.80	2.172	2.060	2.86
29	2-OH-5-Me acetophenone tsc Cu(II)o-phen	2.158	2.064	2.47	2.160	2.060	2.66
30	2-OH-5-Me propiophenone tsc Cu(II)o-phen	2.170	2.061	2.78	2.162	2.061	2.65
31	2-OH-5-Cl acetophenone tsc Cu(II)o-phen	2.156	2.063	2.47	2.156	2.063	2.47
32	2-OH-5-Cl propiophenone tsc Cu(II)o-phen	2.152	2.061	2.49	2.152	2.060	2.53

[a]tsc = thiosemicarbazone, py = pyridine, pic = picoline, pip = piperidine, mor = morpholine, bipy = bipyridyl, o-phen = o-phenanthroline.

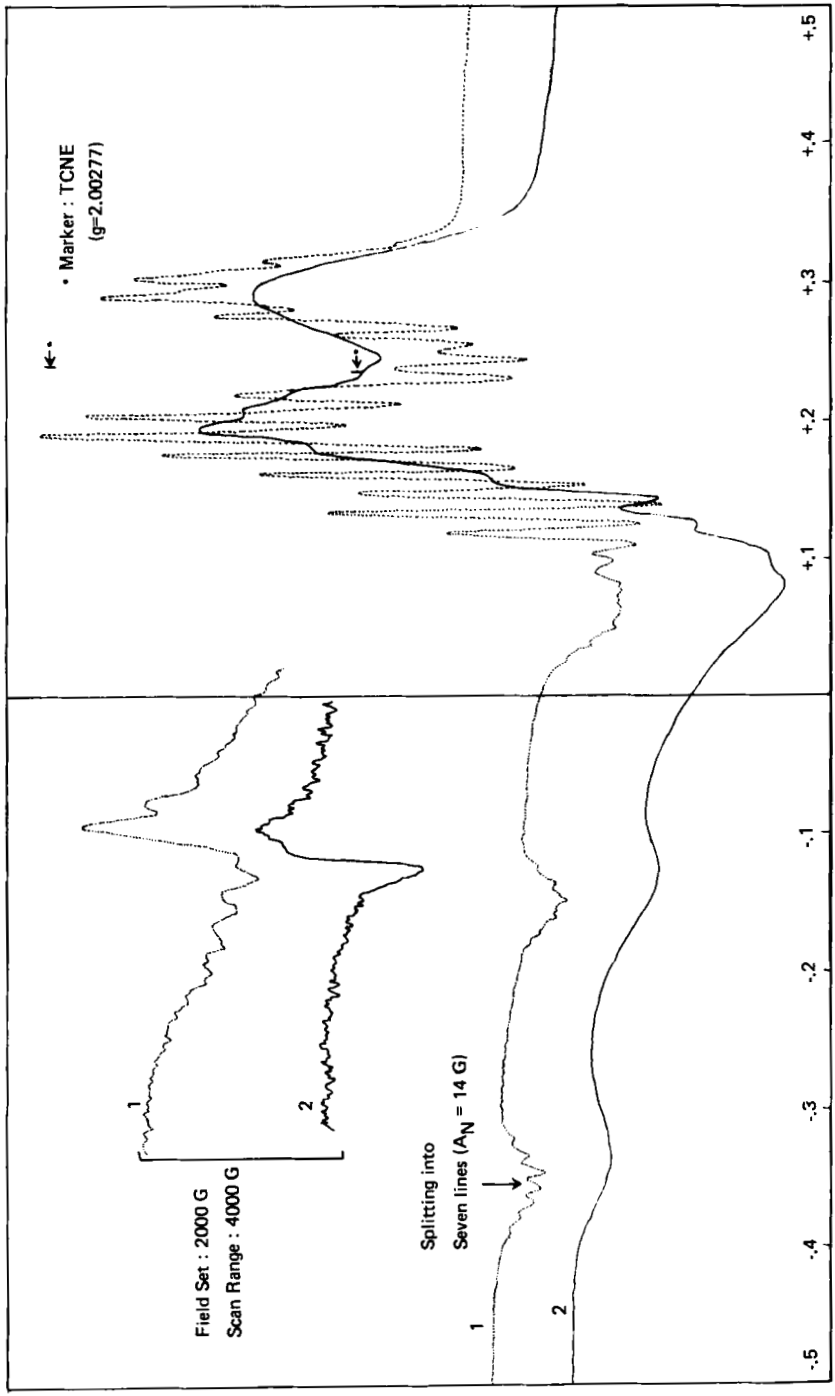

FIG. 1. ESR spectra of (chloroform) (1) 2-OH-5-Cl propiophenone tsc Cu(II)mor and (2) 2-OH-5-Me propiophenone tsc Cu(II)α-pic. Scan range, 1000 G; time constant, 0.064 s; modulation amplitude, 0.63 × 1 G; receiver gain, $1.25 \times 10^4 \times 10$; field set, 3000 G; scan time, 8 min; modulation frequency, 100 kHz; temperature, ~-160°C; microwave frequency, 9.077 GHz.

Downloaded At: 19:58 24 January 2011

REFERENCES

[1] A. V. Ablov and N. V. Gerbeleu, Russ. J. Inorg. Chem., 9, 1260 (1964).
[2] F. A. French and B. F. Freelander, Cancer Res., 18, 1298 (1958).
[3] K. C. Agrawal, P. D. Mooney, and A. C. Sartorelli, J. Med. Chem., 19, 970 (1976).
[4] R. Gromback and S. E. Rasmussen, Acta Chem. Scand., 16, 2325 (1962).
[5] M. Kato, H. B. Jonassen, and J. C. Fanning, Chem. Rev., 64, 99 (1964).
[6] P. W. Anderson, Phys. Rev., 79, 350 (1950).
[7] A. P. Ginsberg, Inorg. Chim. Acta Rev., 5, 45 (1971).
[8] W. E. Hatfield and L. Fred, Inorg. Chem., 5, 1161 (1966).
[9] H. Okawa, T. Tokkii, N. Noraka, Y. Muto, and S. Kida, Bull. Chem. Soc. (Japan), 46, 1462 (1973).
[10] D. J. Hodgson, Inorg. Chem., 15, 3174 (1976).
[11] B. Chiswell, J. R. Gelard, A. T. Philip, and F. Lions, Inorg. Chem., 3, 1272 (1964).
[12] N. C. Mishra, J. Indian Chem. Soc., 55, 839 (1978).
[13] D. V. Ramana Rao and B. Pradhan, Ibid., 58, 733 (1981).
[14] C. B. Mahto, Ibid., 58, 935 (1981).
[15] B. J. Hathaway and D. E. Billing, Coord. Chem. Rev., 5, 143 (1920).
[16] B. J. Hathaway, in Essay in Chemistry (J. N. Bradley and R. D. Gillard, eds.), Academic, New York, 1971, p. 61.

Accepted by editor January 3, 1983
Received for publication February 3, 1983

Downloaded At: 19:58 24 January 2011