

References and Notes

- (1) A. F. Clifford, H. K. El-Shamy, H. J. Emelús, and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953).
- (2) W. A. Sheppard, *J. Am. Chem. Soc.*, **84**, 3058 (1962).
- (3) G. A. Silvey and G. H. Cady, *J. Am. Chem. Soc.*, **72**, 3624 (1950).
- (4) E. A. Tyczkowski and L. A. Bigelow, *J. Am. Chem. Soc.*, **75**, 3523 (1953).
- (5) N. J. Maraschin and R. J. Lagow, *J. Am. Chem. Soc.*, **94**, 8601 (1972).
- (6) N. J. Maraschin, B. D. Catsikis, L. H. Davis, G. Jarvinen, and R. J. Lagow, *J. Am. Chem. Soc.*, **97**, 513 (1975).
- (7) The IR spectra of these materials also showed peaks due to C-F compounds, which may have been CF₃SF₃ and CF₃SF₅. Positive identification was not possible because these materials were present in only small amounts, and the S-F IR region was dominated by SF₄ bands. Separation by GC was not possible since the mixture reacted with the column.

Contribution from the School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

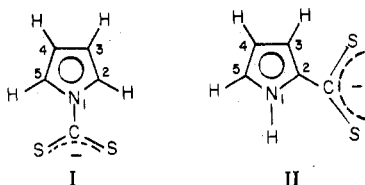
Unusual Oxidation-State Stabilization of Iron Complexes by the Pyrrole-*N*-carbodithioate Ligand

Anton G. El A'mma and Russell S. Drago*

Received April 7, 1977

AIC70258N

The tris(*N,N*-diorganodithiocarbamate)iron(III), [Fe(S₂CNR₂)₃], complexes have been studied extensively¹⁻⁸ because of the considerable interest in the electronic properties of complexes derived from sulfur ligands. The spectral and magnetic properties of a large number of these complexes are very dependent on the nitrogen substituent of the dithiocarbamate^{9,10} and on temperature.^{2,9} These properties have been attributed on the one hand to the R-N-R bond angle⁹ and on the other to the inductive properties of the R substituents.¹⁰ One of the main problems is ascertaining the inductive influence that a substituent exerts. Most investigators have employed the basicity of the parent amine toward a proton as a criterion of electron donation toward the CS₂ group. In this study we report an iron(III) dithiocarbamate with unusual redox properties which is derived from the pyrrole-*N*-carbodithioate ligand (I).¹¹ An improved synthesis



of this ligand is reported as well as the preparation of complexes with Cr(III), Fe(III), and Zn(II). Several of their physical properties related to the metal-ligand interactions have been studied.¹²

Experimental Section

(I) **Syntheses. Sodium Pyrrole-*N*-carbodithioate.** Approximately 1 M solutions of this ligand in Me₂SO were prepared as follows. Sodium hydride¹³ (2.4 g) was reacted with an excess (100 mL) of dimethyl sulfoxide.¹⁴ Freshly distilled pyrrole (7.0 mL) was then added. The resulting pale yellow solution was cooled to 20 °C in an ice bath, and carbon disulfide (6.2 mL) was slowly added. This step is exothermic and yields the deep orange-red solution of the ligand.

Bis(pyrrole-*N*-carbodithioato)zinc(II). Twenty milliliters of a 1 M solution of the ligand was slowly added to a stirred solution of zinc nitrate hexahydrate (3.0 g) in 100 mL of water. The yellow precipitate formed was filtered by suction, washed with water, and crystallized from methanol-water. Anal. Calcd for C₁₀H₈N₂S₄Zn: C, 34.33; H, 2.31; N, 8.0; Zn, 18.70. Found: C, 34.35; H, 2.37; N, 7.96; Zn, 18.51. The green tris(pyrrole-*N*-carbodithioato)chromium(III) was prepared in a similar fashion. It was crystallized from acetone-

Table I. Abbreviations for RR'NCS₂⁻

R	R'	Abbrev	R	R'	Abbrev
CH ₃	CH ₃	ME	C ₂ H ₅	C ₂ H ₅	ET
<i>n</i> -C ₄ H ₉	<i>n</i> -C ₄ H ₉	NBU	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₆ H ₁₃	NHX
<i>i</i> -C ₄ H ₉	<i>i</i> -C ₄ H ₉	IBU	C ₆ H ₁₁	C ₆ H ₁₁	CHX
CH ₃	C ₆ H ₅	MPH	C ₂ H ₅	C ₆ H ₅	EPH
-CH ₂ CH ₂ CH ₂ CH ₂ -		SPYR	-CH=CHCH=CH-		APYR

methanol. Anal. Calcd for C₁₅H₁₂N₃S₆Cr: C, 37.64; H, 2.53; N, 8.78; Cr, 10.86. Found: C, 37.54; H, 2.65; N, 9.06; Cr, 10.96.

Tris(pyrrole-*N*-carbodithioato)iron(III). Anhydrous ferric chloride (1.6 g) was dissolved in 100 mL of methanol and the solution was filtered. Thirty milliliters of a 1 M solution of the ligand was diluted with 10 mL of water and added dropwise to the stirred ferric solution. The almost-black precipitate that formed was filtered by suction, washed with methanol, and air-dried. It was dissolved in the minimum amount of dichloromethane, filtered, and reprecipitated with methanol. Anal. Calcd for C₁₅H₁₂N₃S₆Fe: C, 37.34; H, 2.71; N, 8.71; Fe, 11.57. Found: C, 37.48; H, 2.74; N, 8.74; Fe, 11.53.

(II) **Physical Methods.** Visible spectra were obtained in CHCl₃ solution on a Cary-14 instrument. Infrared spectra were recorded as KBr pellets and Nujol mulls on a Beckman IR-12 spectrophotometer. NMR spectra in CHCl₃ solution were obtained on a Varian Model EM 390B instrument. All chemical shifts were measured relative to internal Me₄Si. Magnetic susceptibilities at ~35 °C in CHCl₃ solution were obtained by the Evans¹⁵ method using Me₄Si as a reference on a Varian T-60 instrument. A concentric NMR tube was used. Solid-state magnetic susceptibilities were obtained at 25 °C using a Gouy balance. [Ni(en)₃]S₂O₃ was used¹⁶ as the calibrant. Electrochemical work was done in acetone (0.1 M in *n*-Bu₄NClO₄ and 10⁻⁴ M in the complex). Potentials were obtained vs. a saturated calomel reference electrode. Mössbauer spectra of powdered samples were obtained at room temperature using a constant acceleration Doppler-shifted ⁵⁷Co source and a 1024 channel analyzer (512 channels were used). Iron foil was recorded for calibration. Spectra were computer-fit using the program PARLORS.¹⁷

Results and Discussion

The ¹H NMR spectrum of Zn(APYR)₂ (see abbreviations in Table I) in CHCl₃ shows two multiplets of equal intensities centered at τ 2.3 and 3.6 ppm. This AA'BB' system is consistent with a structure for the ligand in which the CS₂ is bonded to the nitrogen as shown in structure I. Further evidence for this structure is obtained from the infrared spectrum of the zinc adduct in Nujol which shows the absence of the strong N-H bending and stretching modes which are found at 1146 and 3400 cm⁻¹, respectively, in pyrrole.¹⁸ The infrared spectrum of Fe(APYR)₃ is similar to that of Zn-(APYR)₂ in those two regions, suggesting the same ligand structure. A strong absorption at 1330 cm⁻¹ in the infrared spectra of the zinc and iron adducts is assigned to the coupled C-N stretch of the N-CS₂⁻ residue.¹¹ We were unable to detect by NMR or infrared spectroscopy the isomeric 2-pyrroledithiocarbonylate moiety (II) reported in the synthesis of Kellner et al.¹¹

Table II contains the results from Mössbauer spectroscopy, cyclic voltammetry, and magnetism of Fe(APYR)₃ displayed simultaneously with those of other tris(*N,N*-diorganodithiocarbamate)iron(III) compounds for comparison. The solid-state and solution magnetic moment of Fe(APYR)₃ (~2.2 μ_B) indicates that it is a low-spin species. Ewald et al.⁹ have argued that the trend influencing the magnetic behavior of the ferric dithiocarbamates arises from the differences in the R-N-R bond angle in the coordinated RR'NCS₂⁻. The larger this angle is, the lower is the magnetic moment of that particular ferric dithiocarbamate. This interpretation breaks down since Fe(APYR)₃ has a lower magnetic moment than Fe(CHX)₃ even though the expected CHX-N-CHX bond angle is larger (steric repulsions between the bulky cyclohexyl groups) than the C₂-N-C₅ bond angle of pyrrole¹⁹ (~109°). The isomer shift (δ) of Fe(APYR)₃ is essentially indistinguishable from most of the other iron(III) dithiocarbamates

Table II. Results of Mössbauer Spectroscopy, Cyclic Voltammetry, and Magnetism for Some Iron(III) Dithiocarbamates

No.	Compd	$\mu_{\text{eff.}}^1 \mu\text{B}$		IS (δ), ^{c,s} mm/s	QS (Δ), ^s mm/s	Oxidn potential, ²⁰ V	
		Solid	Soln ^b			Fe ²⁺ /Fe ³⁺	Fe ³⁺ /Fe ⁴⁺
1	Fe(ME) ₃	4.17	4.20 (C)	0.64	0.27	-0.26	+0.58
2	Fe(ET) ₃	4.24	4.41 (C)	0.66	0.26	-0.32	+0.54
3	Fe(NBU) ₃	5.32	4.34 (B)	0.63	0.27	-0.32	+0.55
4	Fe(NHX) ₃	3.52	4.42 (B)	0.62	0.27	-0.33	+0.54
5	Fe(IBU) ₃	3.02	2.88 (B)	0.64	0.27	-0.34	+0.52
6	Fe(CHX) ₃	2.75	2.62 (C)	0.64	0.58	-0.47	+0.41
7	Fe(SPYR) ₃	5.83 ^d	5.82 (B) ^d	0.65 ^d	0.22 ^{d,e}	-0.3 ^d	+0.6 ^d
8	Fe(APYR) ₃	2.19	2.17 (C) ^d	0.62 ^d	0.66 ^d	+0.3 ^{a,d}	+1.3 ^{a,d}
9	Fe(MPH) ₃	2.99	3.33 (C)	0.64	0.55	-0.24	+0.58
10	Fe(EPH) ₃	4.70	3.63 (C)	0.67	0.31	-0.27	+0.58

^a Oxidation potentials referenced to Ag-AgCl-0.1 M LiCl-acetone reference electrode by adding ~0.15 V to the values referenced to the saturated calomel electrode. ^b The (C) and (B) refer to the solvents chloroform and benzene. ^c Relative to sodium nitroprusside. ^d This work. ^e D. Ulrich et al., *J. Inorg. Nucl. Chem.*, 34, 3681 (1972), report values of $\delta = 0.694$ mm/s and $\Delta E_Q = 0.292$ mm/s.

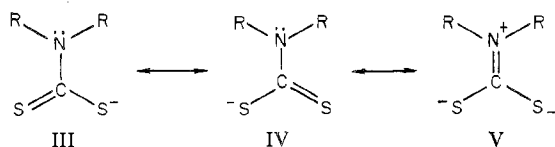
and is the same (within estimated experimental error) as that of Fe(SPYR)₃. Even though Fe(APYR)₃ is very different in many respects from Fe(SPYR)₃, their δ values indicate that there is no measurable difference in the s-electron densities at the respective iron centers. The value of the quadrupole splitting (Δ) of Fe(APYR)₃ at room temperature is the largest of the complexes in Table II. On the Mössbauer time scale, there is rapid exchange between the high-spin and low-spin forms of these complexes. A larger value of Δ is expected for the quadrupole splitting of a low-spin iron(III) compared to a high-spin iron(III) because of the asymmetry of the valence d-electron distribution in the former case. The value of Δ measured for a rapidly interconverting mixture is a weighted average of the two Δ values. The results from Mössbauer coupled with those from the magnetic susceptibility experiment indicate that Fe(APYR)₃ has, at room temperature, the greatest fraction of low-spin Fe(III) of all the compounds indicated.

Like the other tris(*N,N*-diorganodithiocarbamato)iron(III) complexes,²⁰ Fe(APYR)₃ undergoes two reversible electron-transfer reactions at a platinum electrode, i.e.



The redox potentials of the Fe(APYR)₃ system indicate that the ligand "APYR" is dramatically more effective at stabilizing the lower oxidation states than any other dithiocarbamate in Table II and is very different from "SPYR". The potentials needed to form the two species Fe^{III}(APYR)₃ and [Fe^{IV}(CHX)₃]⁺ are similar (Table II).

We are now in a position to attempt to rationalize the observations described above. The following valence bond descriptions have conventionally been employed to rationalize the basicity of dithiocarbamates. Increased contribution from



V is expected from the nitrogen of the more basic amines leading to a more basic sulfur σ donor. As the contribution from form V increases, the effectiveness of the ligand as a π acceptor decreases. Since the nitrogen of pyrrole is expected to be a much poorer electron pair donor toward any acid than that in pyrrolidine, we would expect the contribution from V to be less in APYR than in SPYR. Thus, the low spin state resulting in the large quadrupole splitting in the Fe(APYR)₃ complex must be attributed to effects other than a stronger σ -bonding interaction of iron with a more negatively charged sulfur donor orbital.

The electrochemical results are consistent with a weaker σ -bonding interaction in Fe(APYR)₃ than in Fe(SPYR)₃. A stronger σ -donor interaction would raise the energy of largely metal d_{xy} , d_{yz} , and d_{xz} orbitals because a larger spherical field exists and the metal positive charge is reduced. This makes it easier to oxidize the iron(II) and iron(III) complexes. Experimentally, this is not observed for the APYR complex. The results are consistent with earlier suggestions of extensive metal to ligand π back-bonding.^{10,21} Such an effect would be most pronounced in those systems derived from the most weakly basic amines for which resonance forms III and IV are most important. With increased π back-bonding toward these dithiocarbamates, the d_{xz} , d_{yz} , and d_{xy} orbitals are stabilized, increasing the separation of these orbitals from the largely $d_{x^2-y^2}$ and d_{z^2} orbitals in the complex. This would increase the equilibrium amount of the low-spin form and at the same time make removal of an electron from the highest occupied (essentially metal) orbitals of the complex more difficult.

In order to obtain further support for these arguments, the ligand field strengths of SPYR and APYR were measured by examining the electronic spectra of Cr(SPYR)₃ and Cr(APYR)₃. The ligand field splitting energies²² were found to be 15 540 and 15 980 cm⁻¹, respectively. Unfortunately, we were unable to obtain the Racah parameters for Cr(APYR)₃ because of the presence of a low-energy charge-transfer band in the visible region.

The iron complexes derived from APYR are particularly interesting because they illustrate the very considerable extent to which the redox properties of a transition-metal ion complex can be modified by substituent variation. A pronounced enhancement of the stability of the lower oxidation states of iron results from the pyrrole-*N*-carbodithioate ligand.

Acknowledgment. The authors acknowledge the support of this research by the National Science Foundation. The aid of Dr. David Reichgott with the Mössbauer results and solution magnetic moments is gratefully acknowledged.

Registry No. 7, 21288-86-8; 8, 63765-54-8; Zn(APYR)₂, 61195-93-5; Cr(APYR)₃, 63765-53-7; Na(APYR), 63744-44-5; pyrrole, 109-97-7; CS₂, 75-15-0.

References and Notes

- A. H. White, R. Roper, E. Kokot, H. Waterman, and R. L. Martin, *Aust. J. Chem.*, **17**, 294 (1964).
- G. R. Hall and D. N. Hendrickson, *Inorg. Chem.*, **15**, 607 (1976).
- C. K. Jorgensen, *J. Inorg. Nucl. Chem.*, **24**, 1571 (1962).
- J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature (London)*, **177**, 1042 (1956).
- B. J. McCormick, *Inorg. Chem.*, **7**, 1965 (1968).
- R. M. Golding, W. C. Tennant, C. R. Kanekar, R. L. Martin, and H. White, *J. Chem. Phys.*, **45**, 2688 (1966).
- B. F. G. Johnson, K. H. Al-Obaidi, and J. A. McClevery, *J. Chem. Soc. A*, 493 (1970).
- L. M. Epstein and D. K. Straub, *Inorg. Chem.*, **8**, 784 (1969).
- A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969).

- (10) R. R. Eley, R. R. Myers, and N. V. Duffy, *Inorg. Chem.*, **11**, 1128 (1972).
 (11) R. Kellner, P. Prokopowski, and H. Malissa, *Anal. Chim. Acta*, **68**, 401 (1974).
 (12) R. D. Bereman et al. have reported the synthesis of several transition-metal ions of the same ligand (*Abstracts*, 173rd National Meeting of the American Chemical Society, New Orleans, La., 1977, INOR-64).
 (13) NaH was obtained as a 59% solution in mineral oil. It was washed with petroleum ether and diethyl ether, respectively, prior to use.
 (14) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 8667 (1962).
 (15) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
 (16) N. F. Curtis, *J. Chem. Soc.*, 3147 (1961).
 (17) J. T. Spijkerman, D. K. Sneidiker, F. C. Ruegg, and J. R. Devoe, *Nat. Bur. Stand. (U.S.), Spec. Publ.*, No. 260, 13 (1967).
 (18) R. C. Lord, Jr., and F. A. Miller, *J. Chem. Phys.*, **10**, 328 (1942).
 (19) Bak, Christensen, Hansen, and Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720 (1956); compare Cumpster, *Trans. Faraday Soc.*, **54**, 1266 (1958).
 (20) R. Chant, A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **14**, 1894 (1975).
 (21) F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).
 (22) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

Contribution from the Department of Chemistry,
 University of Nevada, Reno, Nevada 89557,
 the Naval Weapons Center, China Lake, California 93555,
 and the Life Sciences Division, Stanford Research Institute,
 Menlo Park, California 94025

Reactions of Copper(II) and Nickel(II) β -Keto Imine Complexes.¹ 3

Richard P. Eckberg,^{2a} Ronald A. Henry,^{2b} Lewis W. Cary,^{2c}
 and John H. Nelson*^{2a}

Received April 26, 1977

AIC702967

It has been reported³ that Cu(baen), the copper(II) complex of the Schiff base condensation product of 2,4-pentanedione with ethylenediamine, reacts quickly and quantitatively at the methine position with isocyanates to yield mono- or diamides dependent solely on the relative stoichiometry of the reactants. By contrast, the analogous Ni(baen) was found to react very slowly and only with aryl isocyanates to yield only the monoamides. Since these reactions may be regarded as electrophilic substitution reactions,⁴ the marked decrease in the reactivity of Ni(baen) relative to Cu(baen) could be due to the much greater acidity of the methine protons of Ni(baen) as has been found for similar compounds.^{5,6}

If this tenet is correct, then electrophilic reactions with Ni(baen) should occur with more reactive electrophiles, e.g., those which bear strong electron-withdrawing substituents. As part of a continuing research program in this area, the reactions of the electron-deficient electrophiles, *p*-toluenesulfonyl isocyanate (tosNCO, A), diethyl azodicarboxylate (B), and dimethyl acetylenedicarboxylate (C), with Ni(baen) and Cu(baen) have been investigated. The results of these reactions are reported herein.

Experimental Section

Caution! *p*-Toluenesulfonyl isocyanate is toxic and is a powerful lachrymator and should be handled in an efficient fume hood and diethyl azodicarboxylate is potentially a thermally initiated explosive. The electrophiles were obtained from commercial sources and used as received. Solvents were dried by standard procedures. Spectral data were obtained as previously described.^{3,7} Melting points obtained on a Meltemp apparatus are uncorrected. Room-temperature magnetic susceptibilities were determined by the Faraday method using Hg[Co(NCS)₄] as calibrant.⁸ Ligand diamagnetic corrections were calculated from Pascal's constants. Elemental analyses were performed by Chemalytics Inc., Tempe, Ariz. Satisfactory C, H, and N analyses were obtained for all new compounds.

The ligands and their copper(II) and nickel(II) complexes were prepared by published procedures⁹ and purified as previously described.³ All reactions were run in oven-dried glassware in essentially

Table I. Physical Properties of the Compounds

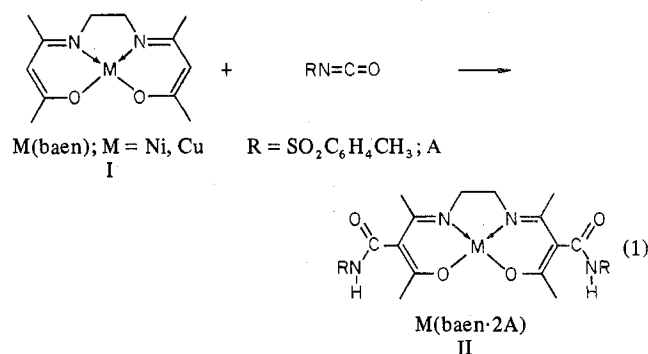
Compd ^a	Mp, °C	% yield	Susceptibility, μ_B (K)	Form and color
Cu(baen-2A)	166-168	98	1.79 (293)	Lavender powder
Ni(baen-2A)-III ^b	146-149	90	Diamagnetic	Brown powder
Ni(baen-2A)-II ^b	111-114	20	Diamagnetic	Red-brown crystals
Cu(baen-2B)	148-150	70	1.79 (294)	Lavender powder
Ni(baen-2B)	159-162	59	Diamagnetic	Orange powder
Cu(baen-2C)	82-85	53	1.86 (296)	Brown powder
Ni(baen-2C)	96-98	40	Diamagnetic	Red crystals
Ni(bapn-B)	142-145	20	Diamagnetic	Red crystals

^a baen \equiv the Schiff base condensation product of 2,4-pentanedione and 1,2-diaminoethane; bapn \equiv the Schiff base condensation product of 2,4-pentanedione and 1,2-diaminopropane; A \equiv *p*-toluenesulfonyl isocyanate; B \equiv diethyl azodicarboxylate; C \equiv dimethyl acetylenedicarboxylate. ^b See text for clarification of structure.

the same fashion. A mixture containing a 2:1 molar ratio of electrophile to complex in dry benzene was stirred magnetically at room temperature in a round-bottom flask fitted with a condenser and a CaCl₂ drying tube. Cu(baen) reacted quickly and exothermically with all three electrophiles while Ni(baen) reacted only at reflux. After 24 h, hexane was added to complete precipitation of the products, which were filtered and washed with hexane. Repeated recrystallizations from benzene/hexane or chloroform/hexane followed by vacuum-drying at room temperature afforded analytically pure samples. Pertinent physical properties of the products are listed in Table I. Ligand displacements were carried out with H₂S in chloroform as previously described.³

Results and Discussion

The reaction of *p*-tosyl isocyanate with Ni(baen) (eq 1)



represents the first example of a complete reaction of an isocyanate with Ni(baen) to yield the diamide product. Previously reported isocyanate reactions between Ni(baen) and isocyanates yielded only the monoamide (R = phenyl, 1-naphthyl).³ As anticipated, the electron-withdrawing ability of the *p*-tosyl group proved sufficient to promote the reaction. Not surprisingly, *p*-tosyl isocyanate reacted quickly and quantitatively with Cu(baen) yielding a product which is very similar in appearance and properties to other diamides³ prepared by reaction of Cu(baen) with isocyanates. The addition of *p*-tosyl isocyanate to M(baen) is formally analogous to its addition to enol ethers to yield β -alkoxyacrylamides.¹⁰ Elemental analyses of the Cu(baen-2A) and Ni(baen-2A) complexes establish that two molecules of tosyl isocyanate added to each molecule of M(baen). The absence of a methine C-H stretch¹¹ (Table II) in the infrared spectra of Cu(baen-2A) and Ni(baen-2A) (for Cu(baen), $\nu_{CH} = 1115 \text{ cm}^{-1}$, for Ni(baen), $\nu_{CH} = 1125 \text{ cm}^{-1}$) confirms that addition occurred at the methine position. However, the two compounds are not isostructural; the presence of amide ν_{N-H} (3150 cm^{-1}) and carbonyl $\nu_{C=O}$ (1595 cm^{-1}) in the infrared spectrum of the copper complex confirms that the bis secondary amide