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STUDIES OF TRANSITION METAL COMPLEXES WITH 2N-QUINOLYL- AND 2N-ISOQUINOLYL-1,1,3,3-TETRAMETHYLGUANIDINES

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Abstract

Ligands derived from 8-quinoline, 6-quinoline, 1-isoquinoline, and 5-isoquinoline were synthesized. These compounds have been used as ligands for complexation of transition metals, such as copper(II) and nickel(II). According to the spectrosocopic data, copper(II) cation forms (1:1) and (1:2) complexes with 2-(8'-quinolyl)-1,1,3,3-tetramethylguanidine and 2-(1'-isoquinolyl)-1,1,3,3-tetramethylguanidine, respectively. In contrast, 2-(6'-quinolyl)-1,1,3,3-tetramethylguanidine and 2-(5'-isoquinolyl)-1,1,3,3-tetramethylguanidine ligands were shown only in (1:1) metal-ligand complex. When these ligands are reacted with nickel(II), the same results are obtained.

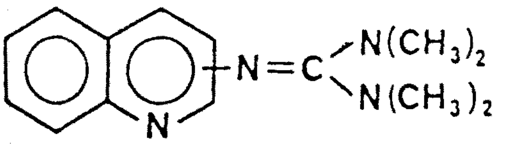
Introduction

A series of 2N-quinolyl- and 2N-isoquinolyl-1,1,3,3-tetramethylguanidines were previously obtained by Foroughifar *et al.* [1]. The basicity of these compounds was also examined by the authors. A variety of these compounds have the ability to chelate several transition metal ions [2-8]. The kinetics of metal ion binding to a series of these compounds has been measured by using several different methods [9-15], and the activation parameters and the mechanism of reactions have also been discussed [16,17].

Schwarzenbach *et al. [18]* have already shown that colored metal complexes may be used as end-point indicators in metal titration and have determined the stability constants of a number of such complexes [18]. The complex forming characteristics of a number of metals with other azo dyes have also been described [19]. The substances which have nearly fulfilled our requirements, however, are 2N-quinolyl- and 2N-isoquinolyl-1,1,3,3-tetramethylguanidines 1 and 2. Pyridine-2-azo-para-dimethylaniline-metal complex formation was used as a model system to examine and discuss the mechanism of biologically important reactions of enzymes containing either Co^{+2} or Zn^{+2} [16]. Also, the above compound appears to be a useful ligand for the study of the kinetics and mechanism of fast metal-ligand substitution processes taking place in aqueous and micellar solutions [11]. A series of 2-phenyl-1,1,3,3-tetramethylguanidines were first synthesized by Kessler and Leibfritz [20], and extended by Leffek *et al.* to study the properties of metal complexing agent [2].

This work seeks to develop a new complexing agent with 2N-quinolyl-1,1,3,3-tetramethylguanidine than the pyridine-2-azo-para-phenyltetramethylguanidine [2]. We decided to synthesize 2N-quinolyl and 2N-isoquinolyl-1,1,3,3-tetramethylguanidine analogue with tetramethylguanidine group substituted for pyridine-2-azo-para-phenyltetramethyl, in the hope that the new compound would have a different ability to bond metal ions than pyridine-2-azo-para-tetramethylguanidine. Therefore, the purpose of the present work is to synthesize transition metal complexes with these compounds.

Keywords: Metal ion complexes; 2N-Quinolyl-1,1,3,3-tetramethylguanidines



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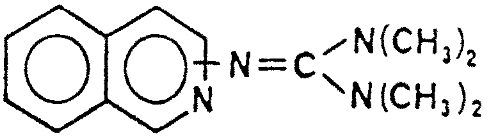

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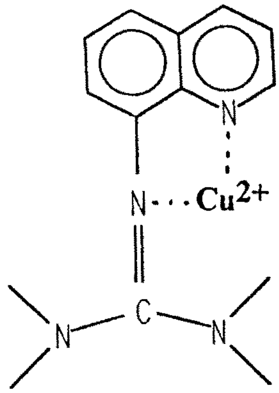
Results and Discussion

The ligands 2N-quinolyl- and 2N-isoquinolyl-1,1,3,3-tetramethylguanidine were synthesized according to a modified procedure by Foroughifar *et al.* [1]. The UV-visible spectra of 2-(8'-quinolyl)-1,1,3,3-tetramethylguanidine in a (1:1) mixture of $CHCl_3$/CH_3CH_2OH show an absorption of 0.08 at 686 nm, and the ligand-copper(II) (1:1) complex has a maximum at the same wavelength. When the concentration of ligand-metal was changed, the complex formed in a ratio of (2:1). The ratio of ligand to metal was obtained using the mole ratio method. The λ_{max} for this complex appears at 842 nm.

In the case of (1:1), with regard to the formation of a five member ring, copper(II) prefers to get lone pair electrons from nitrogen of quinolyl ring, and the reason is: the lone pair electrons of nitrogen in quinolyl substituent are delocalized in the direction of the guanidine group, with comparison to pyridine 2-azo-para-dimethylamine and pyridine-2-azo-para-phenyl-tetramethylguanidine [2,3]. The formation of ligand-metal complex as (1:1) shows a stronger complexing bond than (2:1), because in the case of (1:1) copper(II) withdraws strongly two lone pair electrons from one ligand, whereas when the complex has a ratio of (2:1), the copper(II) gains its electrons from two ligands. This reduces the complexing power and changes λ_{max} from 686 nm to 842 nm.

The IR spectra of the complexes can be discussed in different regions. The M-N appears in the 240-300 cm^{-1} region and might be attributed to the symmetric infrared active M-N stretching vibrations. According to these data, the M-N frequency in ligand-metal complex as (1:1) appears at a higher region than the complex and has a ratio of (2:1) ligand to metal. The above results were confirmed by mass spectrometry.



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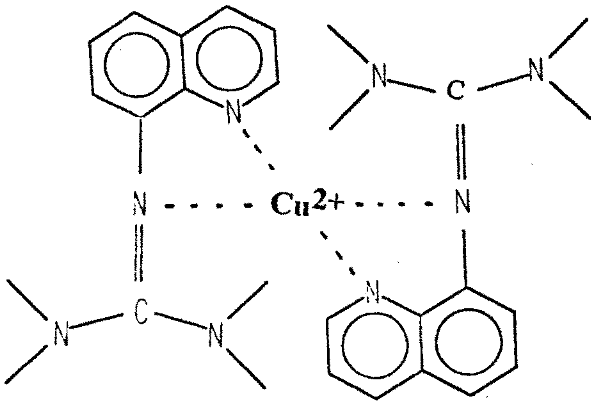

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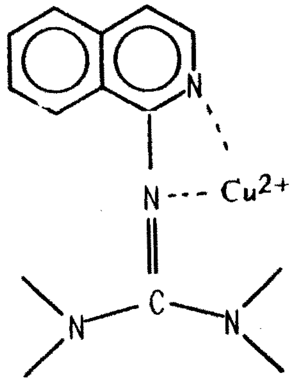
The work was continued to study the behavior of 2-(1'-isoquinolyl)-1,1,3,3-tetramethylguanidine with copper(II) in the same solvent. The ligand showed exactly the same behavior as the 2-(8'-quinolyl)-1,1,3,3-tetramethylguanidine with copper(II) cation.



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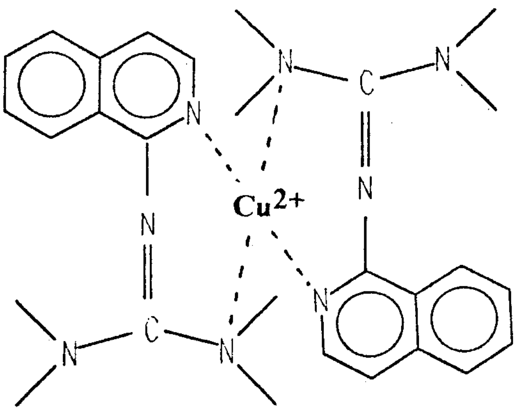

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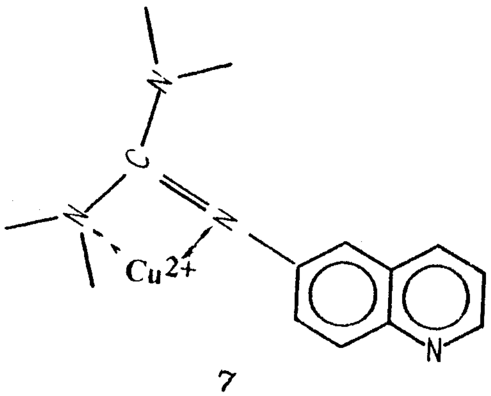
As shown in Table 1, the λ_{max} of structure 5 appeared at 523 nm which is compatible with structure 3. According to these data, metal complex 5 is more stable than metal complex 3. With regard to these results, we decided to study the behavior of two more of these series of ligands. We prepared 2-(6'-quinolyl) and 2-(5'-isoquinolyl)-1,1,3,3-tetramethylguanidine. These compounds were treated with copper(II) cation in CHCl$_3$/CH$_3$CH$_2$OH (1:1) as the solvent at the same condition. The result showed that only a 1:1 metal-ligand complex formed, as we expected. The same conclusion can be reached for nickel(II) cation by these ligands.



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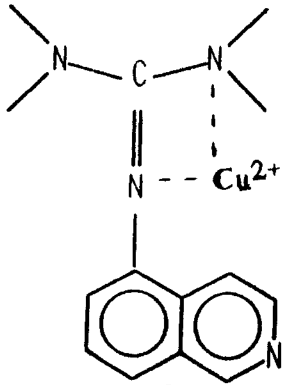

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Experimental Section

Preparation of Ligands

Substituted 2-quinolyl and 2-isoquinolyl-1,1,3,3-tetramethylguanidines were synthesized using a modification of the procedure of Bredereck as previously described [21]. A solution of 1,1,3,3-tetramethylurea (0.1 mol) (Aldrich, dried over 4A molecular sieve) in dry benzene (80 ml) was treated dropwise with a solution of POCl$_3$ (0.2 mol) in dry benzene (40 ml). The reaction was stirred at room temperature for 14 hours and a solution of the appropriate aminoquinoline (0.18 mol) in dry benzene (100 ml) was added in several portions. The reaction mixture was stirred for 20 hours at 75-80°C, after which the solid was separated and washed several times with benzene. The solid was then dissolved in water, and 2N NaOH solution was added to bring the pH to about 14, followed by extraction with benzene, drying over anhydrous sodium sulphate evaporation, and vacuum distillation under reduced pressure. In some cases further purification was carried out by TLC. The amount of POCl$_3$ used was larger than that reported by Bredereck [21] and this increased the yield calculated on the amount of tetramethylurea used.

Preparation of Complexes

50 ml (1:1) of CHCl$_3$C$_2$H$_5$OH and 1 mmol of metal nitrate were added into a 100 ml round-bottom flask. The mixture was stirred for 10 minutes until all of the metal nitrates dissolved. The ligands (1.05 mmol or 2.05 mmol) were added and the temperature maintained at 25°C. After one hour the color changed into dark brown, the product precipitating out of the solution as the reaction progressed.

Spectroscopic Measurements

The ^{1}H and ^{13}C NMR spectra were run in chloroform-d (except where noted) with TMS as the internal standard, using either a Bruker AC 250 FT or a Bruker 100 FT NMR spectrometer. The mass spectra were recorded using Finnigan-Mat TSQ 70 instrument.

The UV-Visible spectra were run in CHCl$_3$/CH$_3$CH$_2$OH (1:1) using a Perkin-Elmer, Lambda 15 UV/VIS spectrometer. The IR spectra were recorded on a Galaxy Series FTIR 5000 Unicam.

2-(8'-quinolyl)-1,1,3,3-tetramethylguanidine ^{1}H NMR: 8.8 (1H, dd, 4.0, 1.5 Hz), 8.0 (1H, dd, 8.0, 1.5 Hz), 7.3 (1H, t, 8.0, Hz), 7.2 (2H, m), 6.9 (1H, d, 8.0, Hz), 2.7 (12H, s), ^{13}C NMR: 161.0, 150.0, 148.0, 142.0, 135.0, 129.0, 127.0, 120.0, 118.0, 118.0, 39.

Mass spec. (rel. int.; %) 242 (100), 198 (89), 154 (60), 142 (20), 128 (16), yield 60%, b.p. 175-180°C at 0.3 torr.

The mass spec. for Cu L (rel. int.; %) 242 (40), 243 (34), 376 (15), 448 (18), 619 (30), 692 (17), and for Ni L complex: 242 (50), 243 (35), 376 (15), 427 (50), 579 (10).

Table 1. Spectroscopic data for ten metal complexes

Ligand	Metal	Concentration Ratio L/M	λ_{max}	M/z	$\nu_{M\text{-}N}$ cm^{-1}
2-(8'-quinolyl)-TMG	Cu^{+2}	1:1	686	376	276
2-(8'-quinolyl), TMG	Cu^{+2}	2:1	842	619	255
2-(8'-quinolyl)-TMG	Ni^{+2}	1:1	591	425	270
2-(8'-quinolyl)-TMG	Ni^{+2}	2:1	667	579	247
2-(6'-quinolyl)-TMG	Cu^{+2}	1:1	756	376	283
2-(6'-quinolyl)-TMG	Ni^{+2}	1:1	709	355	268
2-(5'-quinolyl)-TMG	Cu^{+2}	1:1	--	339	255
2-(5'-quinolyl)-TMG	Ni^{+2}	1:1	638	352	242
2-(1'- isoquinolyl)-TMG	Cu^{+2}	1:1	523	375	293
2-(1'- isoquinolyl)-TMG	Cu^{+2}	2:1	--	619	282

2-(6'-quinolyl)-1,1,3,3-tetramethylguanidine: ^{1}HNMR: 8.7 (1H, dd, 4.0, 1.5 Hz), 8.0 (1H, d, 8.0 Hz), 7.7 (1H, d, 8.0 Hz), 7.2 (2H, m), 7.1 (1H, d, 1.5 Hz), 2.7 (12H, s), ^{13}C NMR: 160.0, 150.0, 147.0, 144.0, 134.0, 130.0, 129.0, 127.0, 120.0, 115.0, 39.0, mass spec. (rel. int.: %) 242 (79), 227 (91), 198 (100), 183 (49), 142 (18), 128 (11), yield 65%, m.p. 60-62°C. The mass spec. for Cu L complex (rel. int.; %) 338 (50), 358 (22), 360 (54), 376 (15), 385 (6), 401 (46), 403 (7). For Ni L complex 335 (100), 380 (70), 415 (28), 2-(5'-isoquinolyl)-1,1,3,3-tetramethylguanidine, ^{1}H NMR: 9.1 (1H, d, 2.5 Hz), 8.4 (1H, d, 2.5 Hz), 7.8 (1H, d, 2.5 Hz), 7.4 (2H, m), 6.8 (1H, t, 2.5 Hz), ^{13}C NMR: 161.0, 152.0, 148.0, 142.0, 131.0, 128.0, 119.0, 117:0, 40.0, 19.0., mass spec. (rel. int. %) 242 (100), 227 (20), 198 (82), 183 (33), 155 (31), 142 (11), yield 60%; b.p. 175-180°C at 0.3 torr. The mass spectra for Cu L complex (rel. int. %) 324 (100), 338 (28), 340 (20), 369 (70), 383 (10), 387 (78), 403 (14), and for Ni L complex 318 (20), 352 (90), 363 (34), 366 (76), 381 (34), 2-(1'-isoquinolyl)-1,1,3,3-tetramethylguanidine: ^{1}H NMR= 8.3 (1H, d, 3Hz), 8.0 (1H, d, 1Hz), 7.5 (3H, m), 7.0 (1H, d, 1Hz), 2.8 (12H, s), ^{13}C NMR: 161.0, 152.0, 148.0, 142.0, 131.0, 130.0, 128.0, 119.0, 118.0, 117.0, 40.0; the mass spec. (rel. int. %) 242 (79), 227 (12), 198 (50), 155 (29), 143 (28), 128 (100), yield 58%, b.p. 170-175°C at 0.3 torr. The mass spectra for Cu L complex (rel. int. %) 242 (50), 243 (100), 362 (12), 364 (52), 425 (20), 427 (50), 619 (10), 692 (5).

Acknowledgements

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