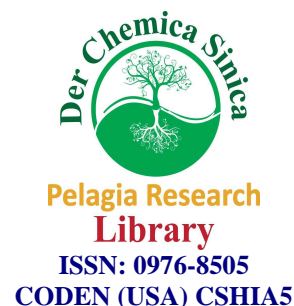




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Mononuclear Copper(I) Complex $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)(\text{CN})]$: Syntheses and Characterization

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ABSTRACT

The mononuclear copper(I) complex $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)(\text{CN})]$ (where $\text{ca}_2\text{en} = N,N'$ -bis(trans-cinnamaldehyde)-1,2-diaminoethane) has been synthesized and characterized by ^1H - and ^{31}P -NMR, FT-IR, UV-Vis spectroscopy and elemental analyses. The ^1H -, ^{31}P -NMR and electronic spectra of the complex are discussed. Cyclic voltammetry of the complex indicates a quasireversible redox behavior.

Key Words: Copper(I) complex, Spectroscopy, Voltammetry.

INTRODUCTION

Copper(I) complexes have long been used in organic synthesis as catalyst for atom transfer [1], photosensitization [2], and the design of supramolecular arrays [3, 4]. Complexes of copper(I) with heteroatomic ligands such as 1,10-phenanthroline exhibit low-lying metal to ligand charge transfer excited states [5]. The chemical and physical properties of transition metal complexes may be controlled by electronic and steric factors [6], which may be modulated by the backbone of the organic ligands. In particular, using steric hindrance, one may promote the tetrahedral coordination mode by excluding octahedral and square-planar coordination geometries around the metal [7]. Although reports on $[\text{Cu}(\text{NN})\text{XY}]$ complexes are numerous [8-10], in the present work, we report the synthesis and characterization of the complex $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)(\text{CN})]$ (Fig. 1).

MATERIALS AND METHODS

Elemental analyses were performed with a Heraeus CHN-O-RAPID instrument. FT-IR spectrum was recorded on a JASCO 680 Plus FT-IR spectrophotometer ($400\text{--}4000\text{ cm}^{-1}$) as KBr pellets. Electronic absorption spectra were recorded on a JASCO V-570 spectrophotometer; λ_{max} (ϵ) are given in nm. ^1H -NMR and ^{31}P -NMR spectra were measured in CDCl_3 with a Bruker ACP-500 spectrometer at 500 MHz. Proton chemical shifts δ_{H} are reported in part per million (ppm)

relative to an internal standard of Me₄Si. Electrochemical data were obtained by cyclic voltammetry using a three electrode cell consisting of a Cu/CuCl reference electrode, a platinum wire counter electrode, and the Pt as a working electrode. Cyclic voltammetric measurements were performed in DMSO with 50 mM sodium perchlorate (NaClO₄) as supporting electrolyte.

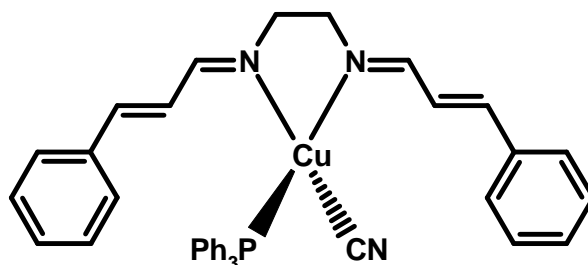


Fig 1 Structure of the copper(I) complex [Cu(ca₂en)(PPh₃)(CN)]

Preparation of [Cu(ca₂en)(PPh₃)(CN)]

The ca₂en ligand was prepared according to the literature method [11]. To a solution of CuCN (89.5 mg, 0.1 mmol) in hot DMSO (10 cm³) a solution of PPh₃ (262 mg, 0.1 mmol) in DMSO (4 cm³) was added dropwise. The mixture was stirred for 10 min and then ca₂en (288 mg, 0.1 mmol) in DMSO (4 cm³) was added and the mixture stirred for an additional 5 min. Slow evaporation of the solvent gave the title compound as red-orange crystals. The crystals were collected by filtration and dried under vacuum. Yield: 531 mg (83%). Anal. Found: C, 73.23; H, 5.60; N, 6.61%. Calcd for C₃₉H₃₅CuN₃P: C, 73.16; H, 5.51; N, 6.56%. IR (ν_{\max} , cm⁻¹): 1626(s, C=N), 2096(s, C≡N); ¹H NMR (DMSO) δ_{H} 3.62 (4H, s, N-CH₂-CH₂-N), 6.92 (2H, d, C=CH-Ph), 7.05 (2H, dd, CH=CH-C), 7.19-7.45 (25H, m, 2Ph-C, PPh₃), 8.01 (2H, d, 2CH=N); δ_{p} -5.444. UV-vis (DMSO) λ/nm 323 (sh, 2520 M⁻¹cm⁻¹), 280 (5400 M⁻¹cm⁻¹).

RESULTS AND DISCUSSION

The *N,N'*-bis(*trans*-cinnamaldehyde)1,2-diaminoethane (ca₂en) ligand was prepared as reported elsewhere [11]. The reaction between triphenylphosphine (PPh₃), copper(I) cyanide and the ca₂en ligand in hot DMSO lead to the formation of the copper(I) mixed ligands complex [Cu(ca₂en)(PPh₃)(CN)]. This complex is stable in air in the solid state for 30 weeks. Its stability in solution depends on the solvent used: while it is stable in acetonitrile solution at room temperature for up to 25 days, it remained unchanged for 7 days in methanol but only 3 days in dichloromethane at 298 K.

FT-IR

The IR spectrum of the free ligand exhibits the characteristic band of an imine, which appears at 1634 cm⁻¹ [11]. This band is shifted to lower frequency in the IR spectra of the complex due to the coordination of the imine nitrogen. The observation of a strong band at 2096 cm⁻¹ in the IR spectrum of complex is assigned to the C-bonded CN⁻ ligand [12,13].

UV-Vis

The UV-Vis spectrum of [Cu(ca₂en)(PPh₃)(CN)] in chloroform exhibits absorption bands at 280 nm ($\epsilon=5400$ M⁻¹cm⁻¹) and at 323 nm (sh, $\epsilon=2520$ M⁻¹cm⁻¹). It is well-known that copper(I) compounds are diamagnetic and colorless, except where the color arises from the anion or charge transfer bands. The most common group of copper complexes contain unsaturated ligands with empty π^* orbitals which can act as electron acceptors [14].

^1H -NMR and ^{31}P -NMR

The ^1H -NMR and ^{31}P -NMR spectra of the complex are shown in Figs. 2 and 3, respectively, and the full spectral data and peak assignments for the complex are presented in the Experimental section. The expected proton resonances of the coordinated ca_2en are observed in the complex, however, the aromatic protons of the coordinated PPh_3 ligand overlap to some extent with those of the Ph-H atoms of ca_2en . Aside from the aromatic protons, which appear at 7.19-7.45 ppm and the two imine protons that appear as a doublet ($\text{HN}=\text{C}$) at ca. 8.02 ppm in the complex, the ethylenic protons appear as a doublet of doublets ($\text{C}=\text{CH}-\text{C}$) at 7.06 ppm and as a doublet ($\text{Ph}-\text{CH}=\text{C}$) at 6.92 ppm [8]. The downfield shift of proton in the complex relative to the free ligand can be rationalized based on the positive charge delocalization onto the corresponding C-atoms through resonance resulting from the coordination of the ligand [8]. The singlet at 3.62 ppm in the complex is assigned to the ($\text{NCH}_2\text{CH}_2\text{N}$) aliphatic protons. The sharp NMR peaks are indicative of diamagnetic Cu(I) complexes. The ^{31}P -NMR spectrum gives a singlet at ca. -5.44 ppm at 298 K [8].

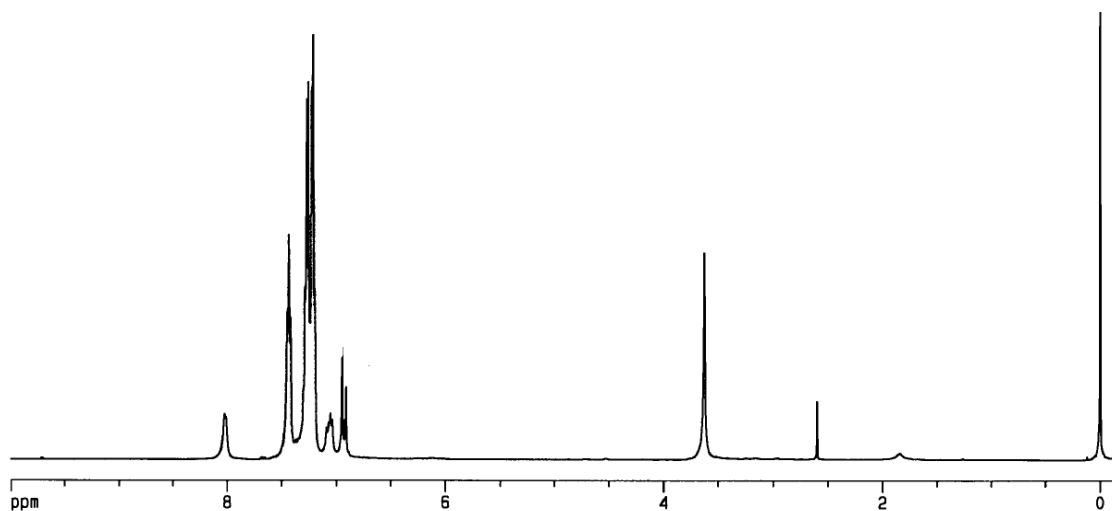


Fig 2 ^1H -NMR spectra of $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)(\text{CN})]$ at 298 K in CDCl_3 solution

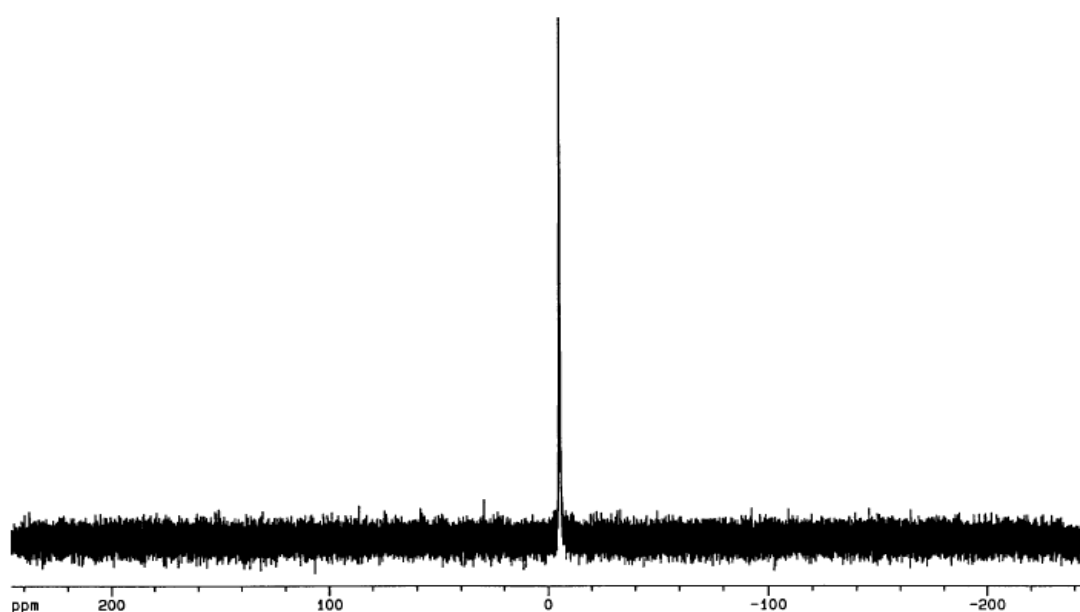


Fig 3 ^{31}P -NMR spectra of $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)(\text{CN})]$ at 298 K in CDCl_3 solution

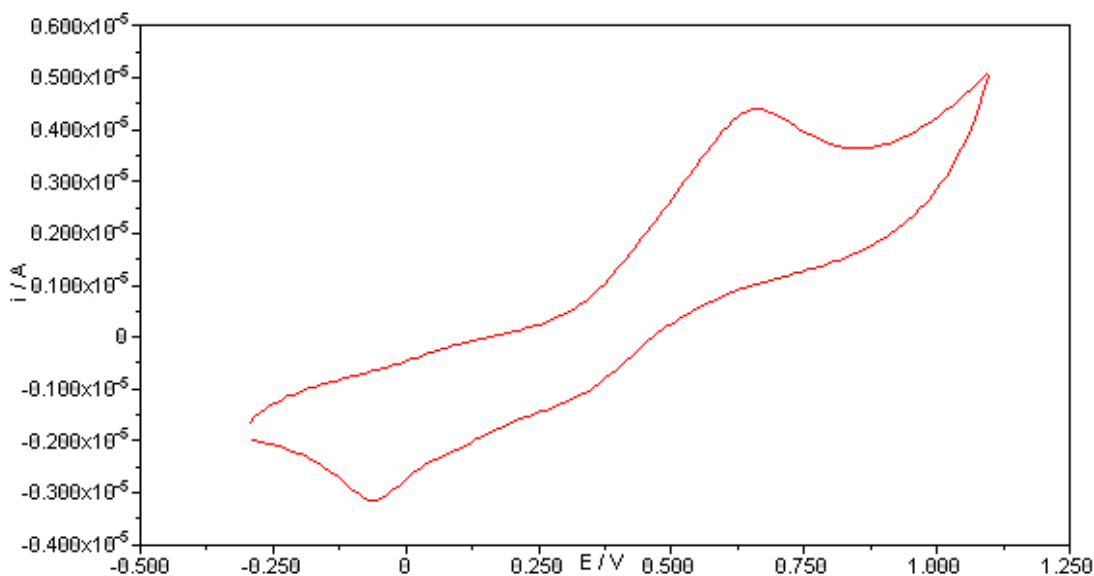


Fig. 4 Cyclic voltammogram of $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)(\text{CN})]$ in DMSO at 298 K.
Scan rate: 50 mV/S

Cyclic voltammetry

The electrochemical behavior of this complex was examined by means of cyclic voltametry in DMSO (Fig. 4). The ligand ca_2en is electroinactive in the working potential region. This complex shows an irreversible $\text{Cu}^{\text{II/I}}$ couple, with the anodic peak ($E_{\text{pa}} = 0.638$ V) and the cathodic peak ($E_{\text{pc}} = -0.056$ V). This is probably due to an irreversible chemical reaction following the electron transfer process [11].

CONCLUSION

The novel copper(I) $[\text{Cu}(\text{ca}_2\text{en})(\text{PPh}_3)(\text{CN})]$ complex containing diimine, phosphine, and pseudohalide CN^- ligands has been synthesized. The ^{31}P - and ^1H -NMR data support the existence of Cu(I) in complex. Solid state FT-IR studies of complex reveal the presence of imine stretching vibrations, occurring at lower frequency owing to coordination to the metal center.

Acknowledgments

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