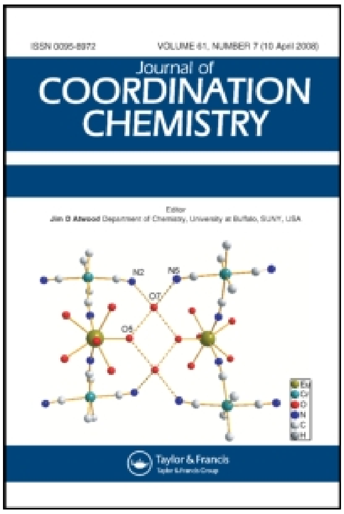

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Stereochemistry of Copper(II) Complexes with Hexacyclen in Solution

Ján Labuda[a]; Mária Van Íčková[a]; Vitaly V. Pavlishchuk[b]; Konstantin B. Yatsimirskii[b]; Mariana I. Mitewa[c]; Panayot R. Bontchev[c]
[a] Department of Analytical Chemistry, Slovak Technical University, Bratislava, Czechoslovakia [b] Institute of Physical Chemistry, Ukrainian Academy of Sciences, Kiev, USSR [c] Department of Chemistry, University of Sofia, Sofia, Bulgaria

To cite this Article Labuda, Ján , Van Íčková, Mária , Pavlishchuk, Vitaly V. , Yatsimirskii, Konstantin B. , Mitewa, Mariana I. and Bontchev, Panayot R.(1990) 'Stereochemistry of Copper(II) Complexes with Hexacyclen in Solution', Journal of Coordination Chemistry, 22: 2, 115 — 120

To link to this Article: DOI: 10.1080/00958979009410034

URL: http://dx.doi.org/10.1080/00958979009410034

J. Coord. Chem. 1990, Vol. 22. pp. 115–120
Reprints available directly from the publisher
Photocopying permitted by license only

STEREOCHEMISTRY OF COPPER(II) COMPLEXES WITH HEXACYCLEN IN SOLUTION

JÁN LABUDA,* MÁRIA VANÍČKOVÁ

Department of Analytical Chemistry, Slovak Technical University, CS-812 37 Bratislava, Czechoslovakia

VITALY V. PAVLISHCHUK, KONSTANTIN B. YATSIMIRSKII

Institute of Physical Chemistry, Ukrainian Academy of Sciences, 252 028 Kiev, U.S.S.R.

MARIANA I. MITEWA and PANAYOT R. BONTCHEV

Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria

(Received February 26, 1990)

The effect of solvent on the behaviour of the copper(II) complex of 1,4,7,10,13,16-hexaazacyclooctadecane (hexacyclen) has been investigated by cyclic voltammetry as well as visible absorption and EPR spectroscopy. Within a series of solvents with different coordination ability (pyridine, DMSO, DMF, water, acetone, acetonitrile) the Cu(II)/Cu(I) reduction potential (about −0.7 V on a mercury electrode and −1.1 V *vs* SCE on platinum), the d–d absorption band (15300 cm^{-1}) and the values of $g_{\perp}$ and $g_{\parallel}$ at −170°C (2.07 and 2.18, respectively) remain unchanged and indicate a stable octahedral CuN_6 environment.

Keywords: Copper(II), macrocycle, stereochemistry, voltammetry, spectroscopy

INTRODUCTION

The relationship between geometric and electronic structures of macrocyclic rings and properties of their metal complexes represents a lasting interest in inorganic and bioinorganic chemistry. The stereochemistry of complexes and equatorial-axial interligand interactions represent such properties.

In investigations of copper(II) axial ligation donors and resulting square-pyramidal coordination geometry (suggested, for example, for the active centre in type 2 copper proteins) the interactions of solvent molecules or monodentate ligands with complexes of multidentate equatorial ligands play an important role.[1,2] For such a study the flexible macrocyclic ligand hexacyclen, [18]aneN_6 (1,4,7,10,13,16-hexaazacyclooctadecane), Figure 1, is of special interest. Its six nitrogen donor atoms, linked by ethylene chains, may form, in the solid state, distorted tetrahedral (below 230 K) or rather rare octahedral (above 250 K) Cu(II) coordination.[3,4] According to ref. 3, the constrained octahedral Cu(II) environment in the $Cu([18]aneN_6)^{2+}$ complex exhibits the most positive redox potential (*i.e.*, the most stable Cu(I) species), among many macrocyclic polyamine Cu(II) complexes.

In the present paper we examine the electrochemical and spectroscopic behaviour of the $Cu([18]aneN_6)^{2+}$ ion in several solvents with different donor properties. The aim of the study was to investigate the stability of complex structure with respect to the apical sites.

---

*Author for correspondence.

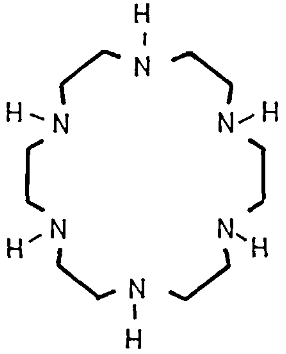

FIGURE 1 The macrocyclic ligand [18]aneN_6

EXPERIMENTAL

[Cu([18]aneN_6)]$(ClO_4)_2$ was prepared from copper(II) perchlorate and hexacyclen. $3H_2SO_4$ (Aldrich) as described previously[5] and checked by analysis. All other chemicals used were of AR grade. The solvents were dried by the usual methods.

Voltammetric measurements were performed with a PA4 polarograph (Laboratórní přístroje, Prague) with a three-electrode arrangement. A platinum microelectrode or a hanging mercury drop electrode were used as the working electrode. A large-surface platinum counter electrode and a saturated calomel reference electrode (aqueous 4 mol dm^{-3} LiCl) with a salt bridge containing the supporting electrolyte in the corresponding non-aqueous solvent were employed. The supporting electrolyte was 0.1 mol dm^{-3} sodium perchlorate. Cyclic voltammograms were recorded in argon atmosphere at a potential scan rate of 0.1 $V s^{-1}$.

Visible absorption spectra were recorded on a Specord M 40 spectrophotometer (Zeiss, Jena). All measurements were performed at 25°C. The EPR spectra were obtained on an ERS 220 (GDR) X-band EPR spectrometer at −170°C (g marker: Mn(II)).

RESULTS AND DISCUSSION

The electrochemical behaviour of Cu([18]aneN_6)$^{2+}$ was investigated by voltammetric studies in six solvents (pyridine, DMSO, DMF, water, acetone, CH_3CN) using a stationary platinum or mercury microelectrode. In some other solvents (CH_3OH, nitrobenzene, CH_2Cl_2) difficulties due to low solubility of the complex were encountered.

With cathodic polarization of the working electrode the complex undergoes a one-electron redox change. The peak potential, E_{pc}, does not in practice depend on the solvent used (Table I). Ferrocene was used as an internal standard both to evaluate the number of electrons involved in the electrochemical process and to assign the potential values. On the platinum electrode the ferrocenium/ferrocene couple exhibits a potential separation of ΔE_p = 80 mV and an i_{pc}/i_{pa} current ratio equal to one with $E_{1/2}$ = 0.37 V *vs* SCE.

TABLE I
Electrochemical data for the $[Cu([18]aneN_6)](ClO_4)_2$ reduction (E_{pc}) and re-oxidation (E_{pa}) processes in various solvents.[a]

Solvent	Peak potential, V					
	Platinum electrode			Mercury electrode		
	E_{pc}	$E_{pa\ 1}$	$E_{pa\ 2}$	E_{pc}	$E_{pa\ 1}$	$E_{pa\ 2}$
pyridine	−1.10	−0.60		−0.74	−0.55	
DMSO	−1.06	−0.35	+0.10	−0.81	−0.79	+0.05
					−0.50	+0.15
DMF	−1.10	−0.40	+0.10	−0.74	−0.60	+0.05
					−0.50	+0.15
water	−1.13	−0.30	−0.02	−0.78	−0.45	−0.05
					−0.24	
acetone	−1.00	−0.60		−0.71	−0.58	−0.28
		−0.40				
acetonitrile	−1.15	−0.40	−0.15	−0.74	−0.30	−0.22

[a] 0.1 mol dm^{-3} $NaClO_4$ supporting electrolyte, potential in V *vs* 4 mol dm^{-3} LiCl SCE, potential scan rate 0.1 V s^{-1}, errors ± 0.01 V.

The $Cu([18]aneN_6)^{2+}$ reduction is diffusion controlled as follows from the linearity of the peak current dependence on the square root of the potential scan rate in the range of $v = 0.05–0.5$ V s^{-1}. Cathodic pathways are evidently the same on both working electrodes used. In contrast to the data given in ref. 3, ($E_{1/2} = -0.44$ V *vs* SCE on the mercury electrode), the reduction potentials found were about −0.7 V (this value is near to that of −0.624 V published in ref. 6). On the voltammograms obtained with the mercury electrode a small cathodic peak or prepeak occurs between −0.46 to −0.56 V (−0.46 V in water). This peak is only about 10% of the main peak current and is not, therefore, considered to result from a complex redox step.

The cyclic voltammograms showed that the redox change for the Cu(II) complex is not reversible (Fig. 2). A cathoanodic system given by E_{pc} and an anodic counter-peak potential, E_{pa1}, is characterized by values of $\Delta E_p > 100$ mV and $i_{pa}/i_{pc} < 0.5$. On the anodic part of the cyclic voltammograms there are also peaks (in Table I reported as E_{pa2}) which reflect chemical changes after the reduction step. The maximum current of these peaks strongly increases when the electrode potential at the cathodic scan is held at the E_{pc} value for several seconds or when the electrode is polarized to −1.5 V. In some cases, especially with the platinum electrode in DMSO, DMF and CH_3CN, the anodic peak at E_{pa2} has the shape of a stripping peak and indicates the oxidation of copper metal. This assignment was confirmed by cyclic voltammograms of copper(II) perchlorate. The voltammetric pattern of $Cu([18]aneN_6)^{2+}$ shows that the corresponding Cu(I) complex persists in solution on the time scale of the cyclic voltammetric experiment but it is nevertheless unstable and undergoes decomposition. Such a process is quite common for many mononuclear Cu(II) complexes and leads to liberation of Cu^+(solv) which is reduced to Cu^0 at a potential more positive than the E_{pc} value of the initial Cu(II) complex.[7] The small anodic peak at +0.15 V on Figure 2, curve b, probably corresponds to the oxidation of Cu^+(solv).[7]

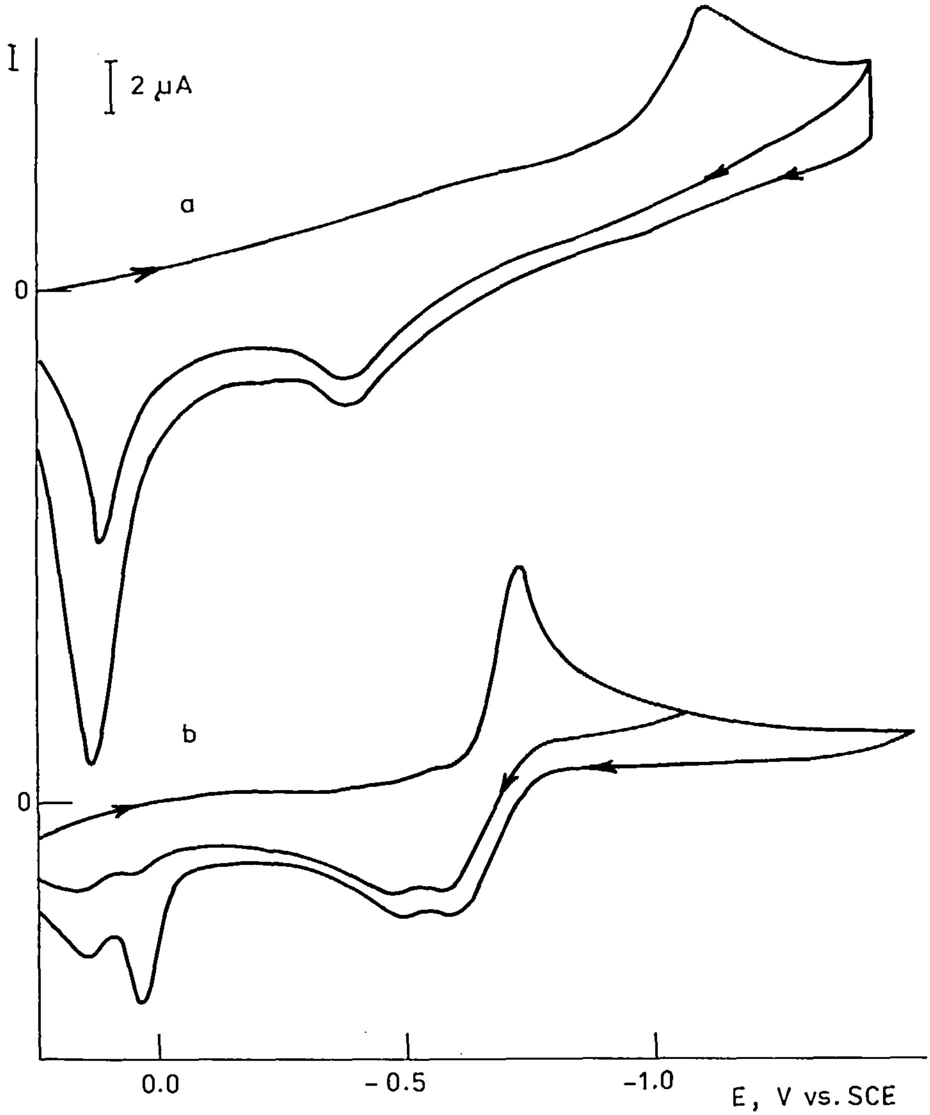

FIGURE 2 Cyclic voltammograms recorded with a platinum microelectrode (a) and hanging mercury drop electrode (b) in a DMF solution of [Cu([18]aneN$_6$)](ClO$_4$)$_2$ (1.2 × 10^{-3} mol dm^{-3}) and NaClO$_4$ (0.1 mol dm^{-3}); scan rate: 0.1 V s^{-1}.

It is clear that there is no simple relationship between the Cu(II) reduction potential and coordination ability of the solvent, conveniently expressed by Gutmann's donor number, DN.[8] The difference in E_{pc} values starting from pyridine to acetonitrile are negligible when compared to those observed for the planar Cu(II) complex with the tetraazamacrocyclic ligand TAAB[2] or with ethylenediamine and β-diketonate derivatives[9] where the E_{pc} change is 200 to 400 mV. The voltammetric behaviour of Cu([18]aneN$_6$)$^{2+}$ can be explained on the basis of the assumption that the Cu(II) coordination environment is stable and virtually the same in all media examined.

The visible absorption spectra also showed the unusual stability of the complex geometry within the given solvent series. In all cases the d–d absorption band is situated at the relatively low ν_{max} value of 15300 cm^{-1}, which means that the Cu(II) chromophore may be assigned to octahedral coordination rather than square planar.[10]

It is generally known that there is some uncertainty in any correlation between visible absorption spectra, electrochemical parameters obtained in solution and Cu(II) coordination number and stereochemistry, regarding the actual Cu(II) species present in solution. Visible absorption spectra provide little information on Cu(II) stereochemistry and are usually useful only for closely related series of ligands or solvents. The redox behaviour of the complexes is determined, in addition to stereochemistry, by the nature of donor atoms as well as σ-donor and π-acceptor properties of ligands. Combination of spectroscopic and electrochemical techniques in different media can give more complete information.

Additional structural information for Cu([18]aneN$_6$)$^{2+}$ is provided by EPR data in solution (Table II). These data are in agreement with a supposition of octahedral structure for the complex in solution. It is evident that, as with solid [Cu([18]aneN$_6$)](BF$_4$)$_2$, the relation $g_\parallel > g_\perp$ is valid, typical for a distorted octahedral structure[4] and the corresponding $g_\perp$ and $g_\parallel$ values obtained for the complex dissolved in different solvents are the same within the limits of experimental error. This fact strongly suggests the absence of adduct formation between the complex and the solvent. It is well documented[11,12] that such adduct formation is typical for planar Cu(II) complexes but unusual for octahedral Cu(II) complexes where no free coordination sites are present.

TABLE II
EPR data for [Cu([18]aneN$_6$)](BF$_4$)$_2$ at −170°C.

Solvent	$g_\perp$ (±0.01)	$g_\parallel$ (±0.01)
pyridine	2.08	2.20
HMPA	2.07	2.18
DMSO	2.07	2.18
DMF	2.07	2.18

The data presented here may be considered as a confirmation of the Cu([18]aneN$_6$)$^{2+}$ octahedral geometry and the stability of this Cu(II) environment through a series of solvents with different donor properties.

REFERENCES

1. Y. Fukuda, A. Shimura, M. Mukaida, E. Fujita and K. Sone, *J. Inorg. Nucl. Chem.*, 36, 1265 (1974).
2. J. Labuda, V. Plaskoň and V.V. Pavlishchuk, *Inorg. Chim. Acta*, **146**, 13 (1988).
3. K. Miyoshi, H. Tanaka, E. Kimura, S. Tsuboyama, S. Murate, H. Shimizu and K. Ishizu, *Inorg. Chim. Acta*, 378, 23 (1983).
4. M.I. Mitewa, P.R. Bontchev, D.R. Vassileva, K.S. Kabassanov, E.N. Zhecheva and D.R. Machandjiev, *J. Coord. Chem.*, **17**, 287 (1988).

5. M.I. Mitewa, P.R. Bontchev, E. Zhecheva, D. Mechandjiev, K. Kabassanov and D. Vassileva, *Inorg. Chim. Acta*, **134**, 17 (1987).
6. M. Upadhyay, S. Gangopadhyay and D. Banerjea, *J. Ind. Chem. Soc.*, **62**, 1029 (1985).
7. P. Zabello, A. Cinquantini, P. Guerriero, S. Tamburini and P.A. Vigato, *Inorg. Chim. Acta*, **117**, 91 (1986).
8. K. Burger, "Solvation, Ionic and Complex Formation Reactions in Non-aqueous Solvents", (Akadémiai Kiadó, Budapest, 1983).
9. J. Labuda, K. Mafune and Y. Fukuda, *Bull. Chem. Soc. Jpn.*, in press.
10. B.J. Hathaway, *Essays Chem.*, **2**, 61 (1971).
11. Y.Y. Chen, D.E. Chu, B.D. McKinney, L.J. Willis and S.C. Cummings, *Inorg. Chem.*, **20**, 1885 (1981).
12. L.G. McDonald, D.H. Brown and W.E. Smith, *Inorg. Chim. Acta*, **63**, 213 (1982).