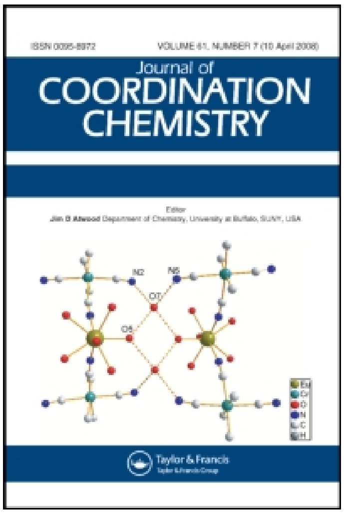

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SPECTRAL AND ELECTROCHEMICAL STUDIES OF THE COPPER(II) COMPLEXES OF TWO MACROCYCLIC LIGANDS

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To cite this Article Lindoy, Leonard F. , Tokel, Nurhan E. , Anderson, Larry B. and Busch, Daryle H.(1971) 'SPECTRAL AND ELECTROCHEMICAL STUDIES OF THE COPPER(II) COMPLEXES OF TWO MACROCYCLIC LIGANDS', Journal of Coordination Chemistry, 1: 1, 7 — 16

To link to this Article: DOI: 10.1080/00958977108070738

URL: http://dx.doi.org/10.1080/00958977108070738

J. Coord. Chem., 1971, Vol. 1, pp. 7–16

Printed in Woking, England

SPECTRAL AND ELECTROCHEMICAL STUDIES OF THE COPPER(II) COMPLEXES OF TWO MACROCYCLIC LIGANDS

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(*Received October* 28, 1970)

Copper(II) complexes of the types $Cu(CR)(ClO_4)_2.H_2O$, $[Cu(CR)X](ClO_4).nH_2O$ (where X = Cl, Br, I and $n = 1$; X = NCS, $n = 0$), $[Cu(CRH)](ClO_4)_2.H_2O$ and $[Cu(CRH)X](ClO_4)$ (where X = Cl, Br, I) have been prepared. The ligands CR and CRH are the related four nitrogen-donor macrocycles 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17), 2, 11, 13, 15-pentaene and *meso*-2, 12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17), 13,15-triene, respectively. All the compounds have the normal magnetic moments expected for Cu(II) complexes with $S = \frac{1}{2}$. Conductance studies in methanol show that the halo-perchlorate complexes are formally five coordinate. The probable structures of the complexes in both the solid and solution are discussed in terms of their visible, infrared and e.s.r. spectra, as well as on the basis of data obtained from conventional polarography and cyclic voltammetry.

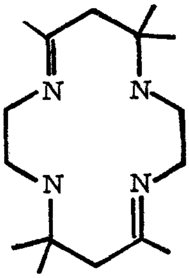
INTRODUCTION

Only a few copper(II) complexes of nitrogen macrocyclic ligands have been described although such complexes are generally quite easily prepared.[2] This is particularly surprising in view of the extensive recent interest in copper(II) complexes of open-chain amine ligands.[3] Apart from the copper derivatives of phthalocyanine and porphyrin,[2,3] perhaps the most studied macrocyclic complexes are those of the Curtis macrocycles **1** (1,7-CT) and **2** (1,4-CT).[4] These, as well as the copper complexes of their fully saturated derivatives, have been studied recently by several workers. No similar studies have been reported for the copper complexes of the related ligands **3** (CR) and **4** (CRH) but the behavior of these ligands with nickel,[5–7] cobalt[8] and iron[9] has been investigated. In the present paper, the results of a study of copper complexes of both these ligands is reported.

EXPERIMENTAL

2,6-Diacetylpyridine (Aldrich Chemical Co.) was recrystallized before use and 3,3′-diaminodipropylamine (Aldrich Chemical Co.) was used as supplied. All other chemicals used for syntheses were of reagent grade.

Visible and near infrared spectra were obtained on a Cary Model 14 recording spectrophotometer either using methanol solutions or Nujol mulls spread on filter paper. Infrared spectra were obtained with a Perkin-Elmer Model 337 spectrophotometer using Nujol or halocarbon mulls.



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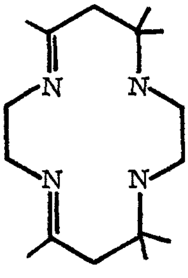

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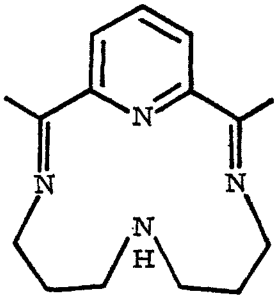

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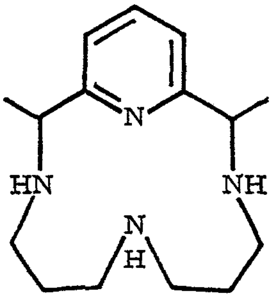

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Conductivity measurements were determined with an Industrial Instruments Inc. conductivity bridge using a cell with platinized electrodes. Magnetic moments were determined by the Faraday method on a balance to be described in a later publication. Diamagnetic corrections were calculated from Pascal's constants. The e.s.r. spectra were obtained on polycrystalline samples at ambient temperature using a Varian Model E-3 EPR Spectrometer. Elemental analyses were performed by the Galbraith Analytical Laboratory. Analytical results are listed in Table I. Conventional polarography was performed with a Controlled Potential and Derivative Voltammeter capable of electrolysis in a three-electrode configuration (Indiana Instrument and Chemical Corporation, Model ORNL–1988A). The recorder was a Hewlett-Packard/Moseley Division X–Y recorder (Model 2D2M). Both a dropping mercury electrode (dme) and a rotating platinum electrode (rpe) driven by a 600 rpm synchronous motor (Welch Scientific Co.) were used as working electrodes. For cyclic voltammetry, both hanging mercury drop (HMDE) and platinum microsphere electrodes (PMSE) (0.13 cm in diameter) were employed. Measurements in methanol were made in conjunction with a saturated aqueous calomel reference electrode (SCE) and a KCl-Agar bridge. Unless otherwise stated, the polarographic studies were carried out on solutions that were $5 \times 10^{-4} M$ in electroactive species. Tetraethylammonium perchlorate (0.05 *M*) (in one instance tetramethylammonium chloride) was used as the supporting electrolyte. The sample and reference compartments of the polarographic cell were connected by a bridge containing an aqueous solution (0.05 *M*) of the respective electrolyte. Apart from those studies in which the effects of temperature on potentials and diffusion currents were investigated, the measurements were made at 25 ± 0.2°C utilizing a controlled temperature water bath. For a typical experiment, oxygen-free nitrogen was passed first through an activated copper column to absorb the last trace of oxygen. The nitrogen was then bubbled through the polarographic solution (via a pure solvent bubbler) for twenty-five minutes to remove dissolved oxygen. After twenty-five minutes the nitrogen flow was diverted so that it only passed over the surface of the cell solution during the duration of the polarographic determination.

TABLE I

Analytical data for the new compounds

Complex	Color	%	C	H	N
$[Cu(CR)](ClO_4)_2 \cdot H_2O$	dark blue	Calcd.	33.4	4.5	10.4
		Found	33.4	4.3	10.3
$[Cu(CR)Cl]ClO_4 \cdot H_2O$	mid blue	Calcd.	37.9	5.1	11.8
		Found	37.9	4.7	11.5
$[Cu(CR)Br]ClO_4 \cdot H_2O$	mid blue	Calcd.	34.7	4.7	10.8
		Found	35.1	4.8	10.6
$[Cu(CR)I]ClO_4 \cdot H_2O$	brownish green	Calcd.	31.8	4.3	9.9
		Found	31.6	4.1	10.0
$[Cu(CR)NCS]ClO_4$	dark blue-grey	Calcd.	40.1	4.6	14.6
		Found	40.5	4.6	14.7
$[Cu(CRH)](ClO_4)_2$	purple	Calcd.	34.3	5.0	10.7
		Found	34.4	5.0	10.5
$[Cu(CRH)Cl]ClO_4$	royal blue	Calcd.	39.1	5.7	12.1
		Found	38.9	5.7	12.0
$Cu(CRH)Br]ClO_4$	royal blue	Calcd.	35.7	5.2	11.1
		Found	35.6	5.2	11.0
$[Cu(CRH)I]ClO_4$	mid blue	Calcd.	32.6	4.7	10.1
		Found	32.4	4.7	10.2
$[Cu(1,7\text{-}CT)](ClO_4)_2$	purple	Calcd.	35.5	5.6	10.4
		Found	35.4	6.0	9.8

For the electrochemical work, Baker A.R. methanol was employed without further treatment. The tetraethylammonium perchlorate (Southwestern Analytical Chemicals) was purified by recrystallization from water and dried over P_4O_{10} *in vacuo*. Maxima were suppressed by the addition of 0.1 ml of a 0.02 % solution of Triton X–100 (Rohm and Haas Co.).

2,12-*Dimethyl*-3,7,11,17-*tetraazabicyclo*[11.3.1]-*heptadeca*-1 (17),2,11,13,15-*pentaenecopper(II) perchlorate monohydrate*, [*Cu*(*CR*)](*ClO*$_4$)$_2$·H$_2$O. To 2,6-diacetylpyridine (6.5g) in methanol (10 ml) was added copper chloride 2-hydrate (6.8 g) in water (120 ml). The solution was heated to 65° then 3, 3′-diaminodipropylamine (5.2g) was added followed by acetic acid (5 ml). The temperature was maintained at 65° for 6 hrs, thereafter 40 ml of saturated sodium perchlorate solution was added. The reaction solution was concentrated to 80 ml. The product that formed on cooling was isolated by filtering and recrystallized from water containing excess sodium perchlorate. The dark blue needles were isolated, washed with water then sparingly with alcohol, and dried over P_4O_{10} *in vacuo*; yield 9.4 g.

Preparation of complexes of the type [*Cu*(*CR*)*X*]*ClO*$_4$·*nH*$_2$*O* (where X = Cl, Br, I and *n* = 1; X = NCS and *n* = 0.

[Cu(CR)](ClO$_4$)$_2$·H$_2$O (1 g) and the appropriate lithium salt (1 g) were dissolved in hot methanol (100 ml). To the hot solution was added sufficient either to cause precipitation of the product as the solution cooled. The crystalline products that formed were washed with a methanol/ether solvent mixture and dried over P_4O_{10} *in vacuo*; yields, 0.4–0.7 g. Several of these complexes were slightly hygroscopic.

meso-2,12-Dimethyl-3,7,11,17-*tetraazabicyclo*-[11.3.1]*heptadeca*-1(17),13,15-*triene monohydrate*, *CRH*·*H*$_2$*O* The free ligand was prepared from its nickel complex by the method of Karn and Busch.[6] m.p. Lit. 83–85°, found 83–84°.

[*Cu*(*CRH*)](*ClO*$_4$)$_2$ To 2.5 g CRH·H$_2$O in hot alcohol (70 ml) was added copper perchlorate hexahydrate (4.5 g) in hot alcohol (40 ml). From the purple solution purple crystals of product precipitated. These were washed with alcohol, ether, and dried over P_4O_{10} *in vacuo*; yield, 5.1 g.

Preparation of complexes of the type [*Cu*(*CRH*)*X*]*ClO*$_4$ (*where X* = *Cl*)

[Cu(CRH)](ClO$_4$)$_2$ (1 g) and lithium chloride (1 g) were dissolved in warm methanol (100 ml). To the warm solution was added ether (400 ml) and the resulting solution was kept at 0° for 1 week. At the end of this time royal blue crystals of product were isolated by filtering, washed with a methanol/ether mixture, and dried over P_4O_{10} *in vacuo*; yield, 0.5 g.

X = *Br* [Cu(CRH)](C*l*O$_4$)$_2$ (0.7 g) and LiBr (1 g) were dissolved in hot methanol (200 ml), the solution was concentrated to 40 ml, diluted with ether (400 ml), and let stand. The royal blue crystals that formed were washed with methanol/ether and dried over P_4O_{10} *in vacuo*; yield, 0.5 g.

X = *I* This compound was prepared from lithium iodide by a similar procedure to that used for the bromide. The mid blue crystals were recrystallized from methanol and dried over P_4O_{10} *in vacuo*; yield, 0.4 g.

RESULTS AND DISCUSSION

The reaction of 2,6-diacetylpyridine with certain polyamines in the presence of metal ions has been demonstrated by Curry and Busch[10] to result in the formation of new macrocyclic complexes. The diamagnetic nickel complex of **3** can be prepared by reaction of 2,6-diacetylpyridine with 3,3′–diaminodipropylamine and nickel chloride in an alcohol–water mixture.[6] The reaction solution is kept at 65° for 6 hours and the perchlorate salt precipitates on addition of perchlorate ion. A small amount of glacial acetic acid is added to the reaction mixture and this catalyses the condensation. In a preliminary note, Rich and Stucky[11] also reported nickel and copper complexes of **3** as their tetrachlorozincate salts. A related procedure was used by these workers in which a *N,N*′-dimethylformamide-water solvent mixture was employed. In the present investigation [Cu(CR)](ClO$_4$)$_2$·H$_2$O was prepared by a similar procedure to that used by Karn and Busch for synthesis of the nickel complex.[5, 6]

The infrared spectrum of the copper complex is quite similar to that of its nickel analog and the absence of carbonyl or primary amine stretching modes confirmed that the Schiff condensation had occurred. The presence of water was indicated by a $\nu_{(OH)}$ mode at ~ 3500 cm^{-1}. The $\nu_{(NH)}$ ligand vibration occurs as a sharp band of medium intensity at 3220 cm^{-1}. The ν_3 and ν_4 modes of the perchlorate group give rise to single strong absorptions which are typical of noncoordinated perchlorate. The molar conductivity in methanol of this compound is in the range expected for a 2:1 electrolyte. Titration of a solution of the compound ($0.98 \times 10^{-3}\,M$ in methanol) with tetramethylammonium chloride ($1.97 \times 10^{-2}\,M$ in methanol) gave a distinct 1:1 end point indicating the formation of a formally five-coordinate cation. No tendency towards coordination of a second chloride ion was detected. Complexes of the type $[Cu(CR)X]ClO_4 \cdot nH_2O$, where X = Cl, Br, I, NCS and $n = 0$ or 1 were isolated from methanol solutions of the diperchlorate complex containing a large excess of the appropriate lithium salt. The method of synthesizing these compounds also emphasizes the preference for formation of formally five-coordinated cations.

TABLE II

Infrared and esr data for the complexes

	Infrared Data (cm^{-1})				ESR data[a]	
			ClO$_4$ mode			
	ν_{O-H}	ν_{N-H}	ν_3	ν_4	$g_\perp$	$g_\parallel$
$Cu(CR)(ClO_4)_2 \cdot H_2O$	3560 sh, 3500	3220	1100	625	2.051	2.105
$[Cu(CR)Cl]ClO_4 \cdot H_2O$	3540, 3420	3140	1100	620	2.059	2.193
$[Cu(CR)Br]ClO_4 \cdot H_2O$	3540, 3440	3130	1100	620	—	—
$[Cu(CR)I]ClO_4 \cdot H_2O$	3490, 3420 sh	3130	1100	625	—	—
$[Cu(CR)NCS]ClO_4$	—	3150	1100	620	—	—
$[Cu(CRH)](ClO_4)_2$	—	3230	1110, 1050 1015	620	2.052	~2.19
$[Cu(CRH)Cl]ClO_4$	—	3205	1090	620	—[b]	—
$[Cu(CRH)Br]ClO_4$	—	3210sh, 3120	1090	620	—	—
$[Cu(CRH)I]ClO_4$	—	3120	1110 1070	1090 620	2.051	2.186
Cu β-phthalocyanine	—	—		—	2.050	2.179[c]

Determined on polycrystalline samples. [b]See text. [c]Ref. 28

The free *meso* isomer of the reduced ligand, CRH, was prepared from its nickel complex as described by Karn and Busch.[6] The ligand reacts with copper perchlorate in alcohol to yield $[Cu(CRH)](ClO_4)_2$ which precipitates from the solution as purple crystals. Once again the infrared spectrum was quite similar to that of the nickel analog. However the perchlorate absorption at about 1100 cm^{-1} (ν_3) was split into three components even though the 620 cm^{-1} band (ν_4) was a singlet. The splitting of ν_3 could be the result of crystal effects; however, there remains a strong possibility that the symmetry of the perchlorate group is lowered by coordination to the copper ion. This compound, as well as the similar derivative of CR, probably has a coordination number greater than four. In the latter case, the water molecule may occupy a coordination site. Coordination numbers of five and six are very common for copper(II) compounds.[3] Complexes of the type $[Cu(CRH)X]ClO_4$, where X = Cl, Br, I, were synthesized from $[Cu(CRH)](ClO_4)_2$ by similar procedures to those described for the analogous complexes of CR.

The halo-perchlorate complexes all show strong perchlorate ν_3 modes in the infrared (Table II). In several cases the ν_3 mode at about 1100 cm^{-1} is slightly structured (not shown in Table II) and for $[Cu(CRH)I]ClO_4$ this mode is strongly split. Thus in the solid the symmetries of the perchlorate ions in these complexes are lowered[12] but it cannot be said with certainty that this is the result of coordination. However, weak coordination of perchlorate anions in axial positions of copper complexes is fairly common.[13]

All these halo-perchlorate complexes show molar conductances (Table III) in methanol with values between those expected for 1:1 and 2:1 electrolytes. This is consistent with the presence of coordinated halide in the solid state. The conductance data is most readily rationalized in terms of concentration dependent equilibria involving displacement of coordinated halide by solvent. The simplest case of such an equilibrium is given by

$$[Cu(Ligand)X]^+ + \text{methanol} \longrightarrow [Cu(Ligand)methanol]^{2+} + X^-$$

TABLE III

Magnetic, conductance and visible spectral data

Compound	Magnetic data[a]		Conductance data (in MeOH)	Visible spectra (cm^{-1})[d,e]	
	$10^6\chi_M$	μ_{eff}BM		Solid (Nujol mull)	MeOH solution
$[Cu(CR)](ClO_4)_2 \cdot H_2O$	1410	1.83	147[b](1.96)[c]; 178 (0.98)	15,760	15,050 (138)[f]
$[Cu(CR)Cl]ClO_4 \cdot H_2O$	1450	1.86	107 (2.22); 150 (0.45); 172 (0.22)	16,290	17,100 (160)
$[Cu(CR)Br]ClO_4 \cdot H_2O$	1480	1.87	108 (2.21); 153 (0.44); 169 (0.26)	16,970	17,100 (169)
$[Cu(CR)I]ClO_4 \cdot H_2O$	1870	2.11	166 (0.95); 192 (0.28)	~17,500 sh[g]	~17,500 sh[g]
$[Cu(CR)NCS]ClO_4$	1450	1.85	106 (1.97); 149 (0.40); 162 (0.24)	17,870	17,400 (160)
$[Cu(CRH)](ClO_4)_2$	1400	1.83	154 (3.08)	18,500	17,870 (179)
$[Cu(CRH)Cl]ClO_4$	1450	1.86	85 (2.30); 119 (0.46); 132 (0.28)	16,660	17,250 (230)
$[Cu(CRH)Br]ClO_4$	1420	1.84	125 (1.84); 159 (0.76); 180 (0.38)	16,970	17,240 (260)
$[Cu(CRH)I]ClO_4$	1380	1.82	118 (2.07); 125 (1.38); 140 (0.69)	16,970	16,970 (290)

[a] At 23°C; [b] Molar conductance in $ohm^{-1}cm^2mole^{-1}$; [c] Concentration in mM; [d] Because of the broadness of all the spectral envelopes, the position of the maxima quoted below must be considered approximate; [e] All spectra also exhibit strong absorptions above ~25,000 cm^{-1}; [f] Molar extinction coefficient; [g] Occurred as a shoulder on the "tail" of a band which extended from the u.v. right across the visible region.

At low concentrations several of the complexes exhibit conductances which indicate that an equilibrium, such as that shown above, lies almost completely to the right. Since the ionizing ability of methanol is moderately high, the conductance behavior is not particularly surprising. For those conductances obtained at concentrations of the order of $2 \times 10^{-3}M$ it should be noted that ion-pairing effects (in addition to coordination) could also be of significance.

All the compounds have room-temperature magnetic moments in the range expected for copper(II) with $S = \frac{1}{2}$ (Table III).

A summary of the infrared data is given in Table II. In all cases the secondary amine stretching modes of the ligand give rise to sharp bands of medium intensity at ~3100–3200 cm^{-1}. The spectra of all the complexes of type $[Cu(Ligand)X]\ ClO_4 \cdot nH_2O$ are quite similar to each other with only small shifts in ligand band positions being evident. Each series of spectra shows a characteristic doublet in the 1650–1550 cm^{-1} region; however, for the complexes of CR, the lower energy band is considerably more intense than the higher band. In the complexes of CRH the intensities of these two bands are either similar or the higher energy band is the more intense. The diminution of the lower energy band in the spectra of the complexes of the saturated ligand has been suggested to result from the absence of an imine stretch.[6] The band does not completely disappear since there is a coincidental pyridine ring absorption. The position (2070 cm^{-1}) of the $\nu_{(C\text{-}N)}$ in the spectrum of $[Cu(CR)NCS]ClO_4$ is typical of an N-bonded terminal thiocyanate.[14] Although the $\nu_{(C\text{-}S)}$ band is also diagnostic for the type of thiocyanate present, this absorption could not be assigned with certainty for the present complex. The compounds that contain water all show $\nu_{(OH)}$ modes at ~3500 cm^{-1}. The water is not removed *in vacuo* over P_4O_{10}. Although it seems likely that the water is simply contained in the lattice, the possibility that it is coordinated cannot be discounted and, in fact, the complexes $Cuen_2X_2H_2O$ (en = ethylenediamine; X = Cl, or Br) have both been shown by x-ray analyses to have essentially tetragonal symmetries with the ethylenediamine molecules coordinating around the copper in a planar manner with one axial site occupied by a halide and the other by a water molecule.[15] Alternatively the water could play a similar role to that in $Ni(CR)Br_2H_2O$. The structure of this compound has been determined[16] and the nickel coordination polyhedron is approximately square pyramidal with the four nitrogens forming the basal plane and one bromide occupying the axial position. The water molecule is tightly hydrogen-bound between the coordinated and the free bromide ion.

The visible spectral data are summarized in Table III. Apart from ligand and/or charge transfer transitions above 25,000 cm^{-1}, each spectrum shows a smooth broad envelope of bands with a maximum in the 17,900–15,000 cm^{-1} range. The general appearance of the spectra of all the CR and CRH complexes is similar, suggesting that they have similar stereochemistries.

TABLE IV

Spectral transitions for copper(II) complexes

	Elongated	Compressed
Tetragonal, D_{4h}:	$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2A_{1g} \rightarrow {}^2B_{1g}$
	$\rightarrow {}^2B_{2g}$	$\rightarrow {}^2E_g$
	$\rightarrow {}^2E_g$	$\rightarrow {}^2B_{2g}$
Trigonal bipyramidal, D_{3h}:		
	$^2E' \rightarrow {}^2A'_1$	$^2A'_1 \rightarrow {}^2E'$
	$\rightarrow {}^2E''$	$\rightarrow {}^2E''$
Square pyramidal, C_{4v}:	$^2B_1 \rightarrow {}^2A_1$	
	$\rightarrow {}^2B_2$	
	$\rightarrow {}^2E_1$	

Table IV lists the predicted transitions for complexes whose stereochemistry is tetragonal (D_4h), trigonal bipyramidal (D_3h), or tetragonal pyramidal (C_4v).[17, 18] In all cases either two or three transitions are expected in the visible range. However, as is the case for the present spectra, such transitions are often not resolved and a single broad absorption is observed. The solid state (Nujol mull) spectra are generally similar to the corresponding solution spectra except for small differences in the positions of the respective maxima which presumably arise from crystal packing interactions in the solid and solvation effects in solution. The spectra of the complexes [Cu(Ligand)Cl]ClO$_4$·nH$_2$O [Ligand = CR ($n = 1$) or CRH ($n = 0$)] were both determined at three concentrations over the range 0.4–2.5 × 10^{-3}M. Within experimental error, both spectra are concentration independent. Thus it appears that any equilibrium of the type suggested to account for the conductance data for these compounds does not influence their spectra; viz. the displacement of the chloride ion by solvent does not provide sufficient perturbation of the copper ion to detect spectroscopically. This is in accord with the halide ions occupying an elongated axial position in each of the halide–perchlorate complexes. Because of its rigidity, the nonreduced ligand (CR) will have a strong tendency to coordinate around the copper ion in a planar configuration. Hence an essentially square-pyramidal geometry in which the coordinating anion occupies the axial position appears most likely for each of these complexes. Because of their similar properties, the complexes of the saturated ligand, CRH, probably also have a related structure. Nevertheless, if there is a tendency to distort towards a trigonal bipyramid, this distortion can readily be accommodated by either of the macrocyclic ligands.

Recent attention has been focused on the electrochemical behavior of quadridentate macrocycles containing Cu(II) or Cu(I) as the central metal.[19–22] The polarographic results for a selection of the present complexes using a dme as indicator electrode are summarized in Table V. The number of electrons involved in each electrode reaction was determined by comparison with the diffusion currents for the analogous Ni(II) complexes determined under identical conditions. Even though such comparisons can sometimes lead to error, due primarily to differences in diffusion coefficients, the validity of this procedure for the one-electron reductions was confirmed by Tomes plots[24] of log $i/i_d - i$ vs. $-E$, where all had slopes very close to the theoretical values (59 mV) predicted for a one-electron nernstian process. (See Table V.) Both the Cu(CRH)$^{2+}$ and [Cu(CRH)Cl]$^+$ complexes appear to give two-electron reductions waves in methanol (concentration, 5.10^{-4}M). The reduction occurs at about −0.58 V vs. S.C.E., but the presence of maxima in the rising portions of the reduction waves made exact analysis impossible.

The complexes [Cu(CR)]$^{2+}$ and [Cu(CR)X]$^+$ (X = Cl, Br, I and NCS) in methanol (concentration, 5·10^{-4}M) all gave one-electron reduction waves half-wave potentials between –0·49 and –0.50 V vs. S.C.E. Tomes plots gave slopes of 57–55 mV suggesting the quasi-nernstian nature of the reduction process. Cyclic voltammetric study on Cu(CR)$^{2+}$ and [Cu(CR)Cl]$^+$ verified the one-electron nature of the reduction. All these CR complexes display diffusion-controlled reduction processes, i.e. plots of i_d vs. $h^{1/2}_{\mathrm{Hg_{corr}}}$ give straight lines. Similar behavior was observed for the Cu(CRH)$^{2+}$ complex. However, for the [Cu(CRH)X]$^+$ complexes where higher concentrations (2.32 × 10^{-3}M), were used to ensure nearly complete coordination of X to Cu, persistent maxima rendered the analyses of the polarographic waves unreliable. In no case was the reduction of the imine functions of the CR complexes observed, as they have been for $Ni(CR)^{2+}$ complexes,[23] since these waves (which appear at ~-0.9 V vs. SCE in the nickel compound) are apparently somewhat more cathodic in the copper case and are masked by the discharge of the solvent which occurs at about -1.10 V vs. SCE. Comparison of the results for the CRH and CR complexes substantiates the premise[21] that increasing unsaturation in the in-plane field of a macrocyclic complex makes the first reduction of the metal ion more facile.

TABLE V

Polarographic data obtained with D.M.E.[a]

Complex	$E\frac{1}{2}$[b]V.	Slope[c]mV	Electrode reaction
$Cu(CRH)(ClO_4)_2$	~−0.58	—[d]	$CuL^{2+} + 2e^- \rightarrow CuL^0$
$[Cu(CRH)Cl]ClO_4$	−0.57	—[d]	$CuL^{2+} + 2e^- \rightarrow CuL^0$
$[Cu(CRH)Cl]ClO_4$[e]	—[d]	—[d]	$CuL^{2+} + 2e^- \rightarrow CuL^0$
$[Cu(CR)](ClO_4)_2 \cdot H_4O$	−0.49	62	$CuL^{2+} + e^- \rightarrow CuL^+$
$[Cu(CR)Cl]ClO_4 \cdot H_2O$	−0.49	62	$CuL^{2+} + e^- \rightarrow CuL^+$
$[Cu(CR)Cl]ClO_4 \cdot H_2O$[f]	−0.52	50	$CuL^{2+} + e^- \rightarrow CuL^+$
$[Cu(CR)Cl]ClO_4 \cdot H_2O$[g]	−0.49	61	$CuL^{2+} + e^- \rightarrow CuL^+$
$[Cu(CR)Br]ClO_4 \cdot H_2O$	−0.49	57	$CuL^{2+} + e^- \rightarrow CuL^+$
$[Cu(CR)Br]ClO_4 \cdot H_2O$[e]	−0.50	59	$CuL^{2+} + e^- \rightarrow CuL^+$
$[Cu(CR)I]ClO_4 \cdot H_2O$	−0.49	66	$CuL^{2+} + e^- \rightarrow CuL^+$
$[Cu(CR)NCS]ClO_4$	−0.49	60	$CuL^{2+} + e^- \rightarrow CuL^+$
$[Cu(CR)NCS]ClO_4$[h]	−0.50	63	$CuL^{2+} + e^- \rightarrow CuL^+$

[a] [Complex] = $5 \times 10^{-4}M$, [supporting electrolyte] = $5 \times 10^{-2}M$ $(Et_4N)ClO_4$, unless otherwise stated; Methanol was the solvent in all cases.
[b] $E\frac{1}{2}$ V vs. S.C.E.
[c] Plot of $\log(i/i_d - i)$ vs. $-E$.
[d] Maximum prevents exact analysis of wave.
[e] [Complex] = $2.32 \times 10^{-3}M$.
[f] $5 \times 10^{-2}M$ $(Me_4N)Cl$ supporting electrolyte.
[g] [Complex] = $2.37 \times 10^{-3}M$.
[h] [Complex] = $2.33 \times 10^{-3}M$.

Within experimental error the variation of the coordinating ability of the axial ligand over the range studied does not appreciably effect the electrochemical behavior of the copper ion. This was particularly evident for the complexes of CR whose reduction waves are not complicated by the presence of maxima. The polarograms of several of the complexes were run at two concentrations ($5.0 \times 10^{-4}M$ and ~ $3.3 \times 10^{-3}M$) in order that the results could be correlated with the conductance data. The half-wave potentials are approximately concentration independent demonstrating that the replacement of halide ion by methanol does not significantly affect the ease of reduction. This is also shown by the fact that reduction of $[Cu(CR)Cl]^+$ in the presence of a 100-fold excess of chloride ion ($5 \times 10^{-2}M$ $(CH_3)_4NCl$ electrolyte) changes the half-wave potentials only slightly (30 mV). Under these conditions it is unlikely that there is significant solvolysis compared to that which occurs in the absence of the excess chloride (cf. Table V).

The conclusions from this study are in accord with the conclusions derived from spectroscopic work, i.e. (a) the displacement of the chloride ion by the solvent molecule, as evidenced by the appearance of the wave due to the formation of Hg_2X_2, does not provide sufficient perturbation of the charge density around the copper ion to be detected as a shift in the $E_{1/2}$ for the reduction of Cu(II); (b) The halide ion must occupy an elongated axial position in each of the penta-coordinated copper complexes, since $\Delta E_{1/2} / \Delta[Cl^-]$ is near zero over the range $0 < [Cl^-] < 5 \times 10^{-2}M$.

For comparison, a similar polarographic study was made of the Cu(II) perchlorate of **1**, namely $Cu(1,7\text{-}CT)(ClO_4)_2$. In methanol, two one-electron reduction processes were observed at $E_{1/2}$ of -0.58 V and −0.99 V vs. SCE, respectively. The first wave is due to a nernstian reduction process; the second wave also appears to exhibit a nernstian reduction, but this conclusion is uncertain due to the presence of a pronounced maximum. Owing to solubility limitations in methanol, we were unable to study the analogous copper complex of fully hydrogenated tetraamine derived from **1**. Recently, polarographic studies on these compounds have been carried out in aqueous buffer solution.[20]

The voltammetric data obtained with rpe parallels that obtained using the dme. Once again, the first half-wave potentials for the complexes of the saturated ligand, CRH, are more negative (−0.74 V to −0.76 V vs SCE) than those of the complexes of CR (−0.50V to −0.52 V vs SCE). As before, the variation of axial ligand from methanol through Cl^-, Br^-, I^-, and NCS^- did not markedly affect the positions of the half-wave potentials for the respective complexes.

Cyclic voltammetry at the HMDE and PMSE was applied to a few of the complexes to verify the apparent polarographic reversibility of the reduction processes and to determine whether the reduction products are stable during the time necessary for sweep reversal. Various scan rates between 30.8 V/min and 0.1 V/min were used. Nicholson and Shain[25] have shown that for an ideally nernstian process E_{peak} should not change with the voltage sweep rate v; ip_c / ip_a should equal unity (where ip_c is the cathodic peak current and ip_a the anodic peak current); $\Delta = Ep_a - Ep_c = + 57/n$mV and $ip_c/v\,\frac{1}{2}$ must have a constant value.

Studies were carried out on solutions of $[Cu(CRH)](ClO_4)_2(5.0 \times 10^{-4}M)$, $[Cu(CRH)Cl]ClO_4$ $(5.0 \times 10^{-4}M)$, $[Cu(CR)Cl]ClO_4 \cdot H_2O$ $(5.0 \times 10^{-4}M)$ and $[Cu(CR)Cl]ClO_4 \cdot H_2O$ $(2.35 \times 10^{-3}M)$. A typical cyclic voltammogram $[Cu(CR)Cl]ClO_4 \cdot H_2O$ $(2.35 \times 10^{-3}M)$ is shown in Figure 1.

The cyclic voltammogramic behavior of $[Cu(CR)Cl]ClO_4 \cdot H_2O$ both at (*a*) high and (*b*) low concentrations is characterized by a peak separation of (*a*) 75 mV and (*b*) 80 mV, respectively and by a forward to reverse current ratio of (*a*) 1.00 ± 0.05 and (*b*) 1.00 ± 0.07. These results suggest a quasi-nernstian one-electron reduction process for $[Cu(CR)]^{2+}$ and $[Cu(CR)Cl]^{1+}$. The peak currents ratio indicates that the Cu(I) complex that is produced during the reduction cycle is stable during the time necessary for moderately slow sweep reversal (at least five minutes). The cyclic voltammetry of $Cu(CRH)^{2+}$ suggests that the primary reduction product is at least marginally stable since a partial anodic wave is observed on the reverse scan. On the other hand, $[Cu(CRH)Cl]^+$ undergoes a totally irreversible reduction at the Pt–microsphere electrode.

ESR spectra of polycrystalline samples of several of the complexes were also determined and the spectra were analyzed by the approximate method of Kneubühl.[26] A typical spectrum is given in Figure 2. The compounds listed (Table II) all show two g values and it is evident that all these values (with the exception of the $g_{||}$ value for $[CuCR](ClO_4)_2 \cdot H_2O$ which appears to be anomalously low) are quite close to each other suggesting that the environment of the copper ion does not vary greatly from complex to complex. While it is not surprising that the CR and CRH ligands provide similar in-plane environments, the fact that a change of axial ligand also has little effect supports our previous observations that axial ligands are of minor importance in determining the properties of the central copper ion in these compounds. The domination of the metal ion properties by the in-plane ligand may be a direct consequence of the use of macrocyclic ligands, which, as a partial result of the confining of the donor atoms, will undoubtedly provide a large peturbation of the copper ion.

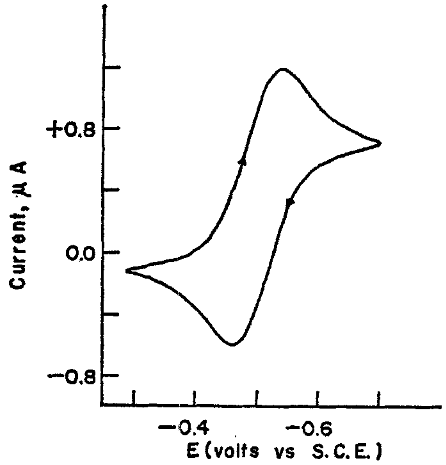

FIGURE 1 Cyclic voltammetry of $2.35 \times 10^2 M[Cu(CR)Cl]ClO_4 \cdot H_2O$ in methanol at HMDE. Scan rate 0.020V/sec.

It has been shown[18, 27] that if the copper ion has a compressed trigonal bipyramidal environment ($^2A_1$ ground state—Table IV), $g_\perp$ should be greater than $g_{||}$ with, theoretically, the latter value being 2.00. A compressed tetragonal environment ($^2A_{1g}$

ground state) would also be expected to give rise to a "reversed" esr spectrum. Since all the present spectra are "normal" with $g_{\|} > g_{\perp}$, it is unlikely that the complexes have either of these stereochemistries.

As discussed earlier, it is most probable that the microsymmetry of the copper ion in most or all of these complexes approximates C_{4v}. Since the physical data suggest that axial ligation effects are slight, it is to be expected that the copper-monodentate ligand bond distances are quite elongated—a situation often found to obtain in other related copper complexes.[3] However, for the present complexes, the effect appears to be so great that an effective symmetry (*as seen by the copper ion*) of approximately D_{4h} is probably more useful for explaining the spectral and electrochemical data. Such a symmetry is also consistent with the esr data and it seems significant that the $g_{\perp}$ and $g_{\|}$ values for our complexes (with the exception noted previously) are all very close to the respective values (Table II) found for Cu β-phthalocyanine whose symmetry is D_{4h}.[28] Nevertheless caution should be exercised since, if exchange coupling is present, the g values listed in the table could differ considerably from the "true" values.[29]

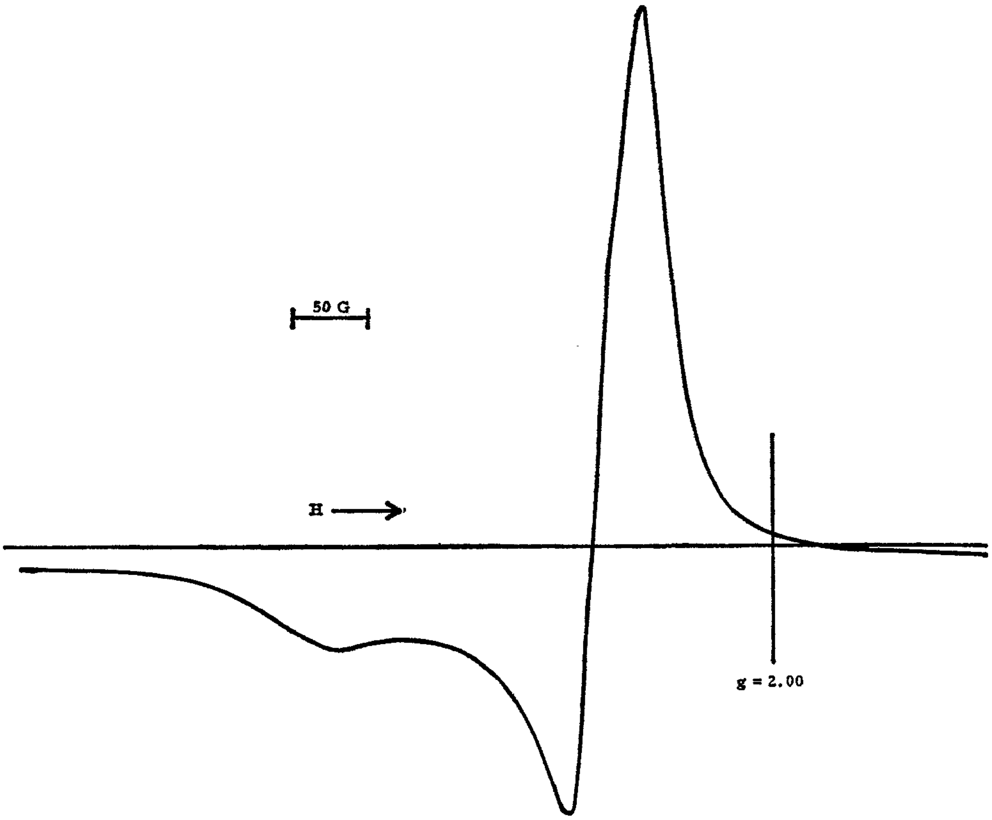

FIGURE 2 ESR spectrum of a polycrystalline sample of [Cu(CRH)I]ClO$_4$

It has been suggested[30] that the $g_{\|}$ value for a compound can be used to give an indication of its covalency. For ionic environments a value greater than 2.3 is usually obtained whereas in more covalent systems the value is expected to be lower than this. Using this criterion all the compounds measured are essentially covalent.

The spectrum (differential) of polycrystalline [Cu(CRH)Cl]ClO$_4$ resembles the other spectra in gross detail but contains a number of additional inflection points which could result from coupling effects. However, in the absence of definite structural data, the analysis of this more complex spectrum is inappropriate.

ACKNOWLEDGEMENT

This investigation was supported by U.S. Public Health Service Grant GM–10040 from the National Institute of General Medical Sciences. We thank Dr. J. Mills for running the esr spectra.

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