

Interaction between Transition Metals and Nucleic Acids. Part III. Synthesis and Structural Studies of Copper(II) Complexes with Schiff Base Ligands Derived from Barbituric Acid

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Abstract

Schiff bases have been prepared from 5-formyl-barbituric acid and 5-formyl-1,3-dimethyl-barbituric acid and various di- or tri-amines. The structures of the corresponding copper(II) complexes have been established by elemental analysis and spectroscopic methods. The molecular structure of one of the complexes, Cu(DiMeBardpt), was determined by X-ray diffraction. Electrochemical study shows that these complexes are reduced at slightly more negative potentials than the corresponding complexes obtained from uracil, which suggests that these new ligands are better electron-donors.

Introduction

In previous papers of this series [1, 2], we reported the synthesis and structural study of Schiff bases derived from 5-formyluracil and their copper(II) complexes. These syntheses were undertaken in order to obtain bifunctional molecules, which, like the antibiotic bleomycin [3], may be able to bind to deoxyribonucleic acids and also form complexes with transition metals capable of activating molecular oxygen, e.g. Fe(II) or Co(II) [4]. By analogy with the proposed mode of action of bleomycin, such compounds might prove useful as anti-tumour agents by inducing single and double strand scissions of DNA. The Urapen-type ligands, which we first synthesized, proved inadequate for two reasons. Firstly, the ligands themselves undergo rapid hydrolysis in water [1] thus preventing biological studies from being made. Secondly, electrochemical data suggested that the Co(II)/Co(III) oxidation potentials were too positive to allow O₂ binding [5]. These two features indicated that the Urapen-type ligands are not good enough as electron donors and that some structural modifications must be introduced to increase both

their resistance to hydrolysis and their electron-donating capacity. Consequently, we decided to replace uracil as the pyrimidine moiety by barbituric and 1,3-dimethylbarbituric acid, which both contain an extra hydroxyl group at C(6). Moreover, barbiturates are known to form complexes with copper(II) [6–8].

In this paper, we report the synthesis and characterisation of the corresponding Schiff base ligands and their copper(II) complexes. The molecular structure of one of the complexes was fully determined by X-ray crystallography. The structures of the other complexes were deduced from their spectroscopic data. Measurements of their half-wave potentials bring support to our assumption that the introduction of the hydroxyl group induces a decrease in the Cu(II)/Cu(I) reduction potential.

Experimental

IR spectra were measured on a Beckman Acculab in KBr pellets. Visible and UV spectra were measured on a Perkin-Elmer Lambda 5. Electrochemical measurements were carried out on a EGG Model 362 Scanning potentiostat using a platinum electrode as the working electrode. The solvent was DMSO, the supporting electrolyte was TEAP, and the concentrations of the solutions were *ca.* 10⁻³ M.

Synthesis of the Ligands

5-formyl-barbituric acid, 5-formyl-1,3-dimethyl-barbituric and 5-acetyl-barbituric acid were prepared as previously reported [6, 7]. 3 mmol of the formyl- or acetyl-barbituric derivative are dissolved in 10 ml of water with 0.41 ml of triethylamine, 1.5 mmol of di- or tri-amine are added and the mixture refluxed for 90 min. The Schiff base precipitates as a white solid which is filtered off, washed with hot water, methanol and ether, and dried under vacuum.

Synthesis of the Complexes

To a suspension of 0.5 mmol of Schiff base in 25 ml of ethanol 95 is added 0.5 mmol of copper acetate. The reflux is maintained for two hours. After cooling the complexes are recovered as green precipitates, except for the square planar ones which are violet.

Crystal Structure of Cu(DiMeBardpt)

Crystal data

$C_{20}H_{27}N_7O_6^{-2}Cu^{2+}$, $M = 525$ orthorhombic, space group $Pbca$, $a = 15.635(6)$, $b = 16.801(6)$, $c = 17.331(7)$ Å, $V = 4552$ Å³, $D_c = 1.53$, $Z = 8$, graphite monochromated Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu(Cu K\alpha) = 17$ cm⁻¹.

A poorly shaped crystal of approximate dimensions $0.2 \times 0.2 \times 0.4$ mm was used for data collection and determination of the unit cell on a Philips PW 1100 diffractometer, using graphite monochromated Cu $K\alpha$ radiation. Parameters values were determined by least-squares refinement of the θ values of 12 well-centered axis reflections.

The data were collected using the $\theta-2\theta$ scan technique with a speed of 0.025° s⁻¹ and a scan-width of $1.3^\circ + 0.2^\circ \text{tg}\theta$. From 3387 independent intensities ($2^\circ < \theta < 60^\circ$), 2244 were considered as observed, their values being greater than $2.5\sigma(I)$ calculated from counting statistics. During the course of the intensity data collection, the crystal showed no loss in intensity due to exposure.

The structure was solved by Patterson and Fourier syntheses. A series of least-squares cycles, with isotropic thermal parameters for all the atoms, reduced the agreement index to $R = 0.12$. The minimized function was $\sum w(|F_o| - |F_c|)^2$ with weights $w = k/(\sigma^2(F_o) + aF_o^2)$ where k and a are variable parameters. An empirical absorption correction [18] was applied reducing the R index to 0.10. Hydrogen atom positions were calculated [$(d_{C-H}) = 1.00$ Å] and added as fixed contributions with isotropic temperature factors equal to that of the attached atoms. A least squares refinement involving anisotropic thermal parameters for the non-hydrogen atoms led to the values of R and R_w of 0.065 and 0.079.

The program used was SHELX 76 [19] with coefficients for analytical approximation to the scattering factors and anomalous dispersion corrections from International Tables of Crystallography. Final atomic coordinates are given in Table I. Distances and angles are listed in Table II. Observed and calculated structural factors and thermal parameters are listed in the supplementary material*.

*Supplementary data available from author C.R.: structural factors, thermal parameters, H-atom co-ordinates, least-squares planes.

TABLE I. Atomic Coordinates ($\times 10^4$) and e.s.d.s

Atom	x	y	z	U
Cu	709(1)	4518(1)	2907(1)	51(1)
N1	-1214(3)	6756(3)	1254(3)	62(7)
C2	-1332(3)	6975(3)	1995(4)	59(8)
O2	-1765(2)	7569(3)	2170(3)	78(7)
N3	-948(3)	6509(3)	2558(3)	52(6)
C4	-422(3)	5873(3)	2388(4)	45(7)
O4	-94(3)	5530(2)	2961(2)	60(5)
C5	-297(3)	5668(3)	1620(3)	49(7)
C6	-719(4)	6103(4)	1020(4)	63(9)
O6	-688(3)	5937(3)	336(3)	109(9)
C7	276(3)	5050(3)	1365(4)	53(7)
N8	724(3)	4593(3)	1793(3)	58(6)
C9	1333(5)	4037(4)	1428(4)	92(10)
C10	2245(5)	4327(5)	1566(5)	144(14)
C11	2489(5)	4440(5)	2381(6)	102(15)
N12	1971(5)	4889(6)	2856(4)	101(13)
C13	-1665(5)	7198(4)	651(5)	90(11)
C14	-1119(4)	6704(4)	3379(4)	79(10)
N1'	-1196(4)	2094(3)	4251(4)	100(9)
C2'	-1321(4)	1997(4)	3483(5)	79(10)
O2'	-1744(3)	1441(3)	3231(3)	83(7)
N3'	-951(3)	2543(3)	3007(3)	59(7)
C4'	-438(3)	3165(3)	3257(4)	58(7)
O4'	-124(2)	3610(2)	2754(2)	55(5)
C5'	-315(4)	3253(4)	4055(4)	73(9)
C6'	-711(5)	2726(4)	4597(5)	94(12)
O6'	-662(5)	2781(4)	5292(3)	126(11)
C7'	223(4)	3851(3)	4377(4)	57(8)
N8'	690(3)	4376(3)	4012(3)	56(6)
C9'	1202(5)	4923(5)	4504(4)	72(11)
C10'	1985(9)	5113(10)	4213(6)	131(32)
C11'	2343(6)	5094(9)	3564(7)	128(26)
C13'	-1568(6)	1511(4)	4779(5)	131(14)
C14'	-1101(4)	2432(4)	2168(4)	65(9)

TABLE II. Bond Distances (Å) and Angles (°) and e.s.d.s

Cu-O4	2.116(4)
Cu-N8	1.934(5)
Cu-N12	2.072(8)
Cu-O4'	2.023(4)
Cu-N8'	1.931(5)
N-C2	1.349(9)
N1-C6	1.401(8)
N1-C13	1.463(9)
C2-O2	1.244(7)
C2-N3	1.387(8)
N3-C4	1.381(7)
N3-C14	1.484(9)
C4-O4	1.257(7)
C4-C5	1.388(9)
C5-C6	1.433(9)
C5-C7	1.442(8)
C6-O6	1.219(9)
C7-N8	1.276(7)
N8-C9	1.476(9)
C9-C10	1.524(11)

(continued on facing page)

TABLE II. (continued)

C10–C11	1.476(13)
C11–N12	1.379(12)
N12–C11'	1.401(14)
N1'–C2'	1.356(11)
N1'–C6'	1.436(9)
N1'–C13'	1.461(10)
C2'–O2'	1.225(8)
C2'–N3'	1.362(9)
N3'–C4'	1.387(7)
N3'–C14'	1.485(9)
C4'–O4'	1.248(7)
C4'–C5'	1.405(9)
C5'–C6'	1.431(10)
C5'–C7'	1.423(9)
C6'–O6'	1.212(10)
C7'–N8'	1.308(8)
N8'–C9'	1.487(9)
C9'–C10'	1.363(16)
C10'–C11'	1.256(17)
O4–Cu–N8	90.0(2)
O4–Cu–N12	109.0(2)
O4–Cu–O4'	103.3(2)
O4–Cu–N8'	92.6(2)
N8–Cu–N12	85.8(3)
N8–Cu–O4'	85.8(2)
N8–Cu–N8'	176.7(2)
N12–Cu–O4'	146.6(3)
N12–Cu–N8'	95.4(3)
O4'–Cu–N8'	91.5(2)
C2–N1–C6	124.4(5)
C2–N1–C13	118.3(5)
C6–N1–C13	117.2(5)
N1–C2–O2	121.7(6)
N1–C2–N3	117.1(5)
O2–C2–N3	121.1(6)
C2–N3–C4	123.0(5)
C2–N3–C14	118.1(5)
C4–N3–C14	118.8(5)
N3–C4–O4	115.4(5)
N3–C4–C5	118.7(5)
O4–C4–C5	125.9(5)
Cu–O4–C4	125.1(4)
C4–C5–C6	120.3(5)
C4–C5–C7	124.0(5)
C6–C5–C7	115.6(5)
N1–C6–C5	116.3(5)
N1–C6–O6	118.9(6)
C5–C6–O6	124.8(6)
C5–C7–N8	126.6(5)
Cu–N8–C7	127.7(4)
Cu–N8–C9	113.2(4)
C7–N8–C9	119.1(5)
N8–C9–C10	109.6(6)
C9–C10–C11	115.6(7)
C10–C11–N12	119.3(8)
Cu–N12–C11	114.8(6)
Cu–N12–C11'	115.6(7)
C11–N12–C11'	114.5(8)
C2'–N1'–C6'	125.1(6)
C2'–N1'–C13'	118.5(6)

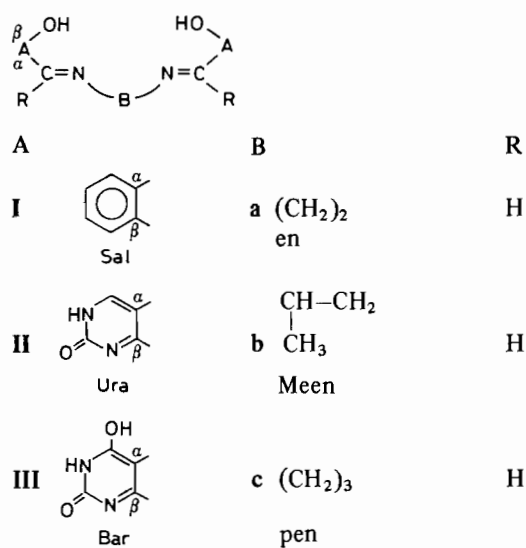
TABLE II. (continued)

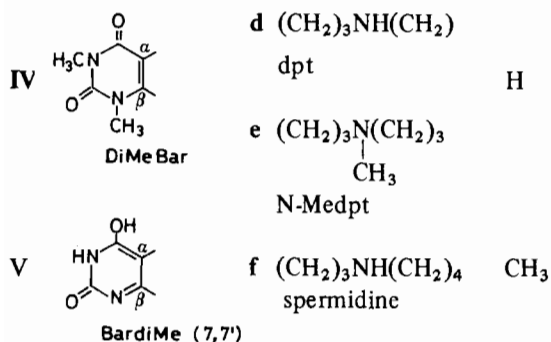
C6'–N1'–C13'	116.4(6)
N1'–C2'–O2'	121.3(6)
N1'–C2'–N3'	116.9(6)
O2'–C2'–N3'	121.8(6)
C2'–N3'–C4'	124.4(5)
C2'–N3'–C14'	116.2(5)
C4'–N3'–C14'	119.4(5)
N3'–C4'–O4'	117.4(5)
N3'–C4'–C5'	117.8(5)
O4'–C4'–C5'	124.8(6)
Cu–O4'–C4'	127.8(4)
C4'–C5'–C6'	121.4(6)
C4'–C5'–C7'	122.8(6)
C6'–C5'–C7'	115.8(6)
N1'–C6'–C5'	114.4(6)
N1'–C6'–O6'	120.3(7)
C5'–C6'–O6'	125.3(7)
C5'–C7'–N8'	128.0(6)
Cu–N8'–C7'	124.8(4)
Cu–N8'–C9'	119.0(4)
C7'–N8'–C9'	116.1(5)
N8'–C9'–C10'	114.6(8)
C9'–C10'–C11'	136.5(13)
N12–C11'–C10'	127.3(12)

Results and Discussion

Synthesis of the Ligands

5-formyl-barbituric acid, 5-formyl 1,3-dimethyl-barbituric acid [9] or 5-acetyl-barbituric acid [10] are condensed with various di- and tri-amines to afford the corresponding Schiff bases **IIIb–f**, **IVb–f**, **Vc–e** in good yields. The ligands with their abbreviated notation are shown below.





The structures of the compounds were established by elemental analysis (Table I) and standard spectroscopic methods (IR, UV and NMR spectroscopy) except for some di-imines which proved not soluble enough to give NMR spectra.

The data are collected in Table III (UV spectra) and Table IV (NMR spectra). From the IR spectra, very little information could be obtained; as already observed for the Schiff bases derived from uracil, the presence of two amide groups and of an imine function leads to a superposition of unresolved bands in the $1720\text{--}1600\text{ cm}^{-1}$ region.

The UV spectra of the pentadentate ligands have λ_{max} at 302 nm, but the tetradentate ligands show

TABLE III. UV-Vis Spectra (nm) and Absorption Coefficients (ϵ) of Ligands and Copper Complexes

Compound	Medium	Ligand	Complex	Reference
IIIb (BarMeen)	DMSO	313(31000) 291(34500)	310(sh) 293(26000) 602(169)	a
IIIc (Barpen)	DMSO	308(27000)	295(16000) 643(123)	a
IIId (Bardpt)	DMSO	301(39500)	—	a
IIIe (BarN-Medpt)	DMSO	301(43500)	303(33500) 650(sh) 760(356)	a
IIIf (Barspermidine)	DMSO	301(53500)	302(36500) 779(206)	a
IVb (DiMeBarMeen)	DMSO	315(31500) 292(38000)	315(sh) 295(29000) 573(332)	a
IVc (DiMeBarpen)	KBr DMSO	312(36500) 295(39000)	545 310(sh) 294(30000) 627(102)	a
IVd (DiMeBardpt)	KBr DMSO	302(47000)	598 302(44000) 749(307)	a
IVe (DiMeBarN-Medpt)	KBr DMSO	320(50000)	738 304(36500) 763(353)	a
IVf (DiMeBarspermidine)	KBr DMSO	302(52000)	757 302(38000) 781(225)	a
Vc (Bardime(7,7')pen)	DMSO	294	—	a
Vd (Bardime(7,7')dpt)	DMSO	299	—	a
Ve (Bardime(7,7')N-Medpt)	DMSO	301	—	a
Cu(Salen)	Nujol		550	14
	CHCl_3		565(433)	14
	DMSO		576(335)	2
Cu(Salpen)	Nujol		581, 518	14
	CHCl_3		595(260)	14
	DMSO		620(185)	2
Cu(Saldpt)	Nujol		1000(sh), 820, 645	14
	CHCl_3		965(200), 813(251)	14
	DMSO		820(275)	2

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TABLE III. (continued)

Compound	Medium	Ligand	Complex	Reference
Cu(SalN-Medpt)	Nujol		950(sh), 815	16
	CHCl ₃		780	2
	DMSO		795(255)	2
Cu(UraMeen)	DMSO		607(230)	2
Cu(Urapen)	DMSO		655(175)	2
Cu(Uradpt)	DMSO		740(385)	2
Cu(UraN-Medpt)	Nujol		900(sh), 760	2
	DMSO		770(330)	2
Cu(Uraspermidine)	DMSO		770(225)	2

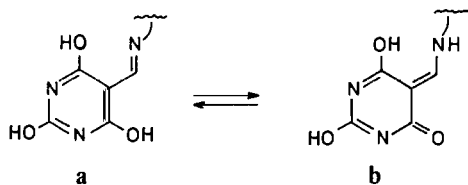
^aThis work.

TABLE IV. Chemical Shifts of Protons in Schiff Bases

Compound	-CH=N	-N-CH ₂ -C	C-CH ₂ -C	N-CH ₃ CH ₃
III _d (Bardpt) ^a	8.2(s)	3.6(t), 2.5(m)	1.72(m)	
III _e (BarN-Medpt) ^a	8.15(s)	3.5(t), 2.34(t)	1.75(m)	2.08(s)
IV _b (DiMeBarMeen) ^b	8.04(m)	3.96(m)		1.28(d), 3.1(s)
IV _d (DiMeBardpt) ^a	8.15(s)	3.6(t), 2.54(t)	1.72(q)	3.1(s)
IV _e (DiMeBarN-Medpt) ^a	8.2(m)	3.55(t), 2.35(t)	1.75(q)	3.1(s), 2.1(s)
V _d (BardiMe(7,7')dpt) ^a		3.5(t), 2.5(t)	1.72(m)	2.6(s)
V _e (BardiMe(7,7')N-Medpt) ^a		3.3(m), 2.39(t)	1.72(m)	2.61(s), 2.14(s)

^aDMSO, TMS as reference 90 MHz. ^bDMSO, TMS as reference 250 MHz.

two maxima at 315 and 295 nm, which suggests that these Schiff bases might be present in solution as a mixture of two isomers [11]: the imine-enol and the enamine-ketone forms **a** and **b**. It should be recalled that in barbituric acid itself only the keto-form is present.



The Schiff bases obtained are stable in water. The presence of the hydroxyl group on the ring thus increases the electron density on the carbon atom of the imine function which does not undergo hydrolysis.

Synthesis of the Copper(II) Complexes

The complexes were obtained by adding a stoichiometric amount of copper acetate to a boiling ethanolic suspension of ligand. The complexes, recovered as green precipitates, were obtained in a reasonably pure state, as shown by elemental analysis (Table V), except for the Schiff bases

derived from 5-acetyl barbituric acid. Different attempts to prepare complexes with these ligands led to products whose analysis revealed an excess or a deficiency of copper. The fact that these complexes could not be obtained in a pure state may be due to the presence of the methyl groups on the imine bonds which sterically interact with the adjacent OH group at C(6) and thus decrease the stability of the complexes. It is relevant to point out that Volpin *et al.* [12] observed distortions in the structure of (Et)Co(7-MeSalen)(en)Br which they attributed to Van der Waals repulsions existing between the methyl group and an adjacent hydrogen atom on the benzene ring. For these reasons, we have limited our study to the complexes of Schiff bases derived from barbituric acid and 1,3-dimethylbarbituric acid.

Crystal Structure of Cu(DiMeBardpt)

Blue crystals of this complex were obtained from a slowly cooling alcoholic solution. The structure is shown in Fig. 1. The ligand occupies five coordination sites of the copper(II) ion which has slightly distorted trigonal-bipyramidal coordination geometry, as evidenced by the angle N(8)-Cu-N(8') of 176.7° whereas the idealized geometry requires 180°. The O(4)-Cu-O(4'), O(4)-Cu-N(12) and

TABLE V. Colours, Analytical Data and Yields for Copper(II) Complexes

Compound	Colours	Analysis ^a				Yields (%)
		C	H	N	Cu	
Cu(BarMeen)·0.75CH ₃ OH·H ₂ O	violet	37.33 (37.77)	3.35 (3.85)	19.20 (19.02)	14.54 (14.38)	87
Cu(Barpen)·0.5CH ₃ OH·H ₂ O	brown	36.79 (37.12)	3.41 (3.53)	18.65 (18.56)	14.08 (14.03)	77
Cu(BarN-Medpt)·CH ₃ OH	emerald-green	40.81 (41.98)	4.86 (4.86)	19.13 (19.04)	11.18 (12.34)	79
Cu(Barspermidine)·0.5H ₂ O	emerald-green	41.23 (41.50)	4.75 (4.47)	19.69 (19.94)	12.75 (12.92)	93
Cu(DiMeBarMeen)·0.25H ₂ O	violet	43.25 (43.22)	4.34 (4.34)	17.35 (17.79)	13.19 (13.45)	90
Cu(DiMeBarpen)	olive-green	43.56 (43.63)	4.38 (4.28)	17.66 (17.97)	13.50 (13.58)	94
Cu(DiMeBardpt)·0.5CH ₃ OH	blue	45.05 (45.51)	5.24 (5.36)	18.20 (18.13)	12.19 (11.75)	74
Cu(DiMeBarN-Medpt)·CH ₃ CH ₂ OH	emerald-green	46.60 (47.22)	5.91 (5.99)	16.71 (16.76)	10.95 (10.86)	82
Cu(DiMeBarspermidine)	emerald-green	46.75 (46.79)	5.40 (5.38)	18.30 (18.20)	12.14 (11.79)	85

^aCalculated values are given in parentheses.

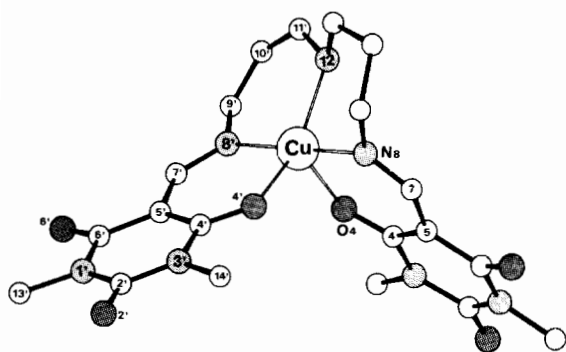


Fig. 1. A perspective view of Cu(DiMeBardpt).

O(4')-Cu-N(12) angles are respectively of 103.3, 109.0 and 146.6° (idealized 120°). The four atoms Cu, O(4), O(4') and N(12) are perfectly planar, N(8), and N(8') being perpendicular to this plane. The pyrimidine ring, O(4), C(7), N(8) and the Cu atoms are approximately in the same plane (mean distance to the least-squares plane: 0.035 Å).

Comparison of this structure with that of Cu mbpN, which was previously reported [13], shows many similarities. Selected distances and angles for Cu(UraN-Medpt) and Cu(DiMeBardpt) are given in Table VI. The geometries around the Cu atom are nearly identical: the Cu, N(8), N(8'), O(4) and O(4') atoms superimposed with a mean distance of 0.06 Å. The main differences between the two structures concern the Cu-O(4) bond distance (2.116(4)

TABLE VI. Selected Distances and Angles of Cu(UraN-Medpt) and Averaged Distances for Cu(DiMeBardpt) e.s.d.s: 0.007 Å (Cu-X), 0.01 Å (C-C, C-O, C-N) and 0.2° for Angles

	Cu(UraN-Medpt) ^a	Cu(DiMeBardpt) ^b
Cu-O(4)	2.089	2.069
Cu-N(8)	1.938	1.932
Cu-N(12)	2.151	2.072
C(4)-O(4)	1.26	1.25
C(4)-C(5)	1.42	1.40
C(5)-C(7)	1.43	1.43
C(7)-N(8)	1.27	1.29
C(5)-C(6)	1.38	1.43
C(6)-N(1)	1.33	1.42
N(1)-C(2)	1.36	1.35
C(2)-O(2)	1.24	1.23
C(2)-N(3)	1.38	1.37
N(3)-C(4)	1.36	1.38
O(4)-Cu-N(8)	91.6	90.0
O(4')-Cu-N(8')		91.5
O(4)-Cu-N(8')	87.8	92.6
O(4')-Cu-N(8)		85.8
O(4)-Cu-O(4')	100.6	103.3
N(8)-Cu-N(8')	179.1	176.7
O(4)-Cu-N(12)	129.7	109.0
O(4')-Cu-N(12)		146.6
N(8)-Cu-N(12)	90.5	85.8
N(8')-Cu-N(12)		95.4

^aSee ref. 2. ^bThis work.

TABLE VII. Torsional Angles of the Amino Dipropyl Chain in Cu(UraN-Medpt) and in Cu(DiMeBardpt) (mean standard deviation: 1°)

	Cu(UraN-Medpt) ^a	Cu(DiMeBardpt) ^b
C(5)-C(7)-N(8)-C(9)	-179	-175
C(7)-C(8)-C(9)-C(10)	107	107
N(8)-C(9)-C(10)-C(11)	74	56
C(9)-C(10)-C(11)-N(12)	-71	-51
C(10)-C(11)-N(12)-C(11')	-178	-167
C(11)-N(12)-C(11')-C(10')	172	-140
N(12)-C(11')-C(10')-C(9')	55	5
C(11')-C(10')-C(9')-N(8')	17	19
C(10')-C(9')-N(8')-C(7')	107	143
C(9')-N(8')-C(7')-C(5')	-178	-179

^aSee ref. 2 ^bThis work.

and 2.023(4) Å) and the conformation of the amino-dipropyl binding chain shown by the torsional angles given in Table VII.

Spectroscopic Studies

UV spectra (Table III)

In the UV spectra of the Cu(II) complexes, λ_{\max} values are not very different from those of the corresponding ligands, but in general a lowering of the molecular extinction coefficient is observed. We must point out that the tetracoordinated complexes present a shoulder at $\lambda = 310$ nm with a λ_{\max} at 295 nm. It probably indicates that, in these complexes, two tautomeric forms similar to those postulated for the ligands (see above) are present [11].

Visible spectra (Table III)

Information on the geometry around the metal can be obtained from the positions of the absorption maxima in the visible-near IR region [13-15]. However, use of spectral data in this case is made difficult because of the width of the major absorption bands. The visible spectra of the complexes are shown in Table III, together with the spectral characteristics of related known complexes, namely complexes of tetra- or penta-dentate Schiff base ligands derived from salicylaldehyde [13, 15]. Comparison of the Nujol (or KBr), CHCl_3 and DMSO spectra reveals no systematic variation in band positions. The geometry around copper must then be similar in the solid state and in solution. The complexes derived from tetradentate ligands have nearly identical spectra with λ_{\max} between 550 and 650 nm. Just like Cu Salen, the complexes having two carbon atoms joining the azomethine linkages must also be square-planar [14]. When the chain contains three carbon atoms, the geometry around the metal is probably slightly distorted towards a tetrahedron,

as in Cu Salpen [14]. As for the complexes with pentadentate ligands, the complete structures of Cu(UraN-Medpt) and Cu(DiMeBardpt) have been determined by X-ray crystallography, so that these compounds can be used as references. The visible spectra of the postulated pentacoordinated complexes are very similar to those of the above complexes, so we can assume that they are five-coordinate with comparable geometry.

From these results, it can be concluded that the Schiff bases derived from barbituric acid form complexes with copper(II) which have geometries similar to those derived from the Urapen-type ligands.

IR spectra

After complexation of the Barpen-type ligands, the frequencies of the C=N and $\begin{matrix} \text{C} \\ \parallel \\ \text{O} \end{matrix}$ -N vibrations are slightly lowered.

For the DiMeBarpen-type complexes, thin and intense bands appear at 1700 cm^{-1} and 775 cm^{-1} with a lowering of the average frequency of the other bands in this region towards *ca.* 1640 cm^{-1} [6-8]. Between 850 and 800 cm^{-1} , a fairly strong band which is always observed in the parent compounds disappears after complexation, whereas a thin band appears at *ca.* 580 cm^{-1} or 530 cm^{-1} for Barpen-type ligands and DiMeBarpen-type ligands, respectively. It may be attributed to the stretching vibration of (Cu-O) [8].

Electrochemical Studies

The electrochemical properties of the copper complexes have been studied in DMSO solution and compared to those of Cu Urapen-type complexes previously reported [2] in order to evaluate the influence of the hydroxyl group at C(6) on the half-wave potential of copper(II). Half-wave potentials have been measured on a rotating platinum electrode, and the values of those and other reference complexes are reported in Table VIII. Cyclic voltammetry

TABLE VIII. Half-wave Potentials $E_{1/2}$ (V, SCE) for Cu(II) Complexes

Complex	$E_{1/2}$
Cu(Salen)	-1.25
Cu(Urapen)	-0.66
Cu(Uradpt)	-0.80
Cu(BarMeen)	-1.05
Cu(Barpen)	-0.82
Cu(Bardpt)	-0.95
Cu(BarN-Medpt)	-0.85
Cu(Barspermidine)	-0.95
Cu(DiMeBaren)	-1.13
Cu(DiMeBarpen)	-0.85
Cu(DiMeBardpt)	-0.90
Cu(DiMeBarN-Medpt)	-0.80
Cu(DiMeBarspermidine)	-0.99

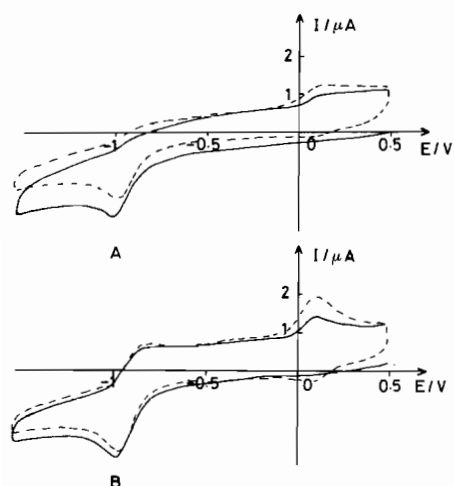


Fig. 2. Cyclic voltammetric curves of Cu(Bardpt) (A) and Cu-(DiMeBardpt) (B). Scan rate: 100 mV s^{-1} , —: first scan, ---: running scans, DMSO, TEAP 0.1 M, complex 0.55 mM.

measurements have also been carried out in the same solvent (Fig. 2) and show that for both complexes the reduction is reversible.

Half-wave potentials

From the values of Table VIII, it can be seen that the Cu(II)/Cu(I) reduction potentials are more negative by ca. 200 mV, for the Barpen than for the Urapen-type complexes, but still not as negative as for the Salen-type complexes. This suggests that the introduction of a hydroxyl group at C(6) produces, as expected, an increase in the electron density at the metal center. Because of the rigid square-planar geometry of Cu(BarMeen) or Cu(DiMeBarMeen), the reduction of copper(II) is more difficult (-1.1 V) than for the pentacoordinated ones (-0.9 V), which, even though they have an extra electron-donating atom, possess a more flexible geometry [17].

Cyclic voltammetry

Cyclic voltammetry at a platinum electrode reveals different behaviour for the two types of complexes, DiMeBar and Bar, which was not the case with linear voltammetry. With the first type of complex, reduction occurs in one step at potentials which are close to the $E_{1/2}$ values observed under stationary conditions (Fig. 2A). Reoxidation of the reduced complexes occurs in three successive steps at -0.85 , -0.45 and $+0.19 \text{ V}$, which suggests that the Cu(I) \rightarrow Cu(II) charge transfer is followed by chemical reactions leading to electroactive species. With the second type of complexes (Fig. 2B), the reduction is still a one-step process but the reoxidation occurs in two steps at more anodic potentials.

Conclusion

We have prepared new tetra- and penta-dentate Schiff bases derived from barbituric acid. The structure of one of the copper(II) complexes has been fully determined by X-ray crystallography. Electrochemical data on the complexes reveal that the presence of an extra hydroxyl group on the pyrimidine part increases, as expected, the electron density on the metal center, as compared to the corresponding Urapen-type complexes. These results suggest that we can obtain cobalt complexes which will be able to bind and activate molecular oxygen [20, 21]. Preliminary results indicate that Co(II) and Co(III) complexes can be synthesized with the same ligands, an X-ray structure determination of one of them being under way, and that they will show catalytic activity in the oxidation of phenols by molecular oxygen.

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