246. Template Synthesis, Crystal Structure, and Spectroscopic Characterization of [*N,N'*-Bis(2-pyridylmethylene)-1,3-diamino-2-methyl-2-nitropropane]copper(II) Perchlorate

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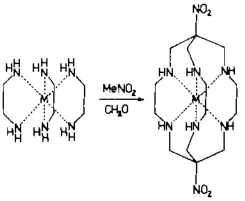
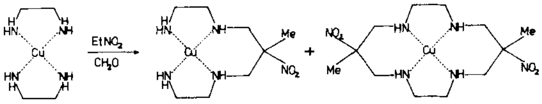
In a facile carbon-acid condensation reaction of bis(2-aminomethylpyridine)copper(II) with nitroethane and formaldehyde in basic MeOH the *N,N'*-bis(2-pyridylmethylene)-1,3-diamino-2-methyl-2-nitropropane)copper(II) cation is produced in essentially quantitative yield. The perchlorate salt crystallizes in space group $P2_1cn$, $a = 9.083(2)$, $b = 15.198(3)$, $c = 16.025(3)$. Cu(II) is essentially four-coordinate, though there are weak axial interactions to the perchlorate O-atoms. There is a large tetrahedral distortion from the least-squares plane through the Cu and four N donors; with the Cu(II) in the plane, N-atoms are up to 0.25 Å above or below. Solution spectroscopy confirms that the solution structure of the cation is qualitatively the same as in the solid. The complex and its precursor have been investigated by room-temperature magnetic-moment measurement, voltammetry, and by IR, electronic, and electron spin resonance spectroscopy.

Introduction. – Within recent years, detailed studies of template condensation reactions involving carbon acids and amine complexes of the inert metal ions Co(III) [1] [2], Rh(III) [3], Ir(III) [4], and Pt(IV) [5] have been reported. With formaldehyde and the carbon acid nitromethane, tris(ethane-1,2-diamine) complexes produce in basic solution in a facile, high-yielding, and stereospecific manner macrobicyclic complexes *(Eqn. 1)* [1]. Similar reactions occur with other carbon acids such as diethyl malonate [6]. The simplicity of these reactions has offered a powerful route to a new range of encapsulating ligands.

Attempts to extend these syntheses to labile metal-ion complexes directly have not been successful, although the free macrobicyclic ligands will encapsulate a wide range of labile metal-ions [7]. One report of a similar condensation involving formaldehyde, ammonia and tris(ethane-1,2-diamine)nickel(II) has appeared, although the yield of macrobicyclic complex is very low indeed [8]. Nevertheless, it is clear that some type of condensations with labile metal-ions occur in reactions of the type of *Eqn. 1*, and it is apparent that facile routes to at least new macromonocyclic and multidentate ligands may be developed. Reactions of labile metal-ion amines with carbon acids and formaldehyde have, therefore, been under detailed scrutiny. Ethane-1,2-diamine complexes of



(1)



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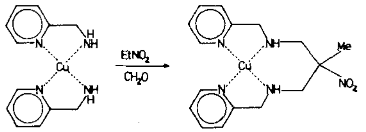


(3)

Cu(II) and Ni(II) with nitroethane and formaldehyde, for example, lead to new ligands *(Eqn. 2)* [9].

With heterocyclic donors *(e.g. Eqn. 3)*, the sites of condensation are limited to one side of the molecule. The number of possible products is, therefore, limited. In addition, the enforced planarity to part of the multidentate ligand may lead to structural distortions of complexes with these ligands similar to the distortions observed *e.g.* in blue Cu proteins. In this paper, we report the synthesis and structural and spectroscopic characterization of the Cu(II) multidentate complex formed from condensation of bis(2-aminomethylpyridine)copper(II) with formaldehyde and nitroethane.

Results. – Reaction of bis(2-aminomethylpyridine)copper(II) ($Cu(pic)_2^{2+}$) with formaldehyde and nitroethane in basic MeOH produces in high yield the tetradentate ligand *N,N'*-bis(2-pyridylmethylene)-1,3-diamino-2-methyl-2-nitropropane) complexed to Cu(II) ($Cu(ndap)^{2+}$). Chromatography of a sample of the isolated product on *SP-Sephadex C-25* resin with 0.25M NaCl solution indicated that within the detectable limit (> 97%), $Cu(ndap)^{2+}$ is the only component. IR spectra of the product have characteristic bands assignable to $\tilde{\nu}_{as}(NO_2)$ (1555 cm^{-1}) and $\tilde{\nu}_s(NO_2)$ (1355 cm^{-1}), in addition to bands associated with the pyridine rings. Both precursor and product have room-temperature magnetic moments fully consistent with d^9 Cu(II) (1.80 and 1.84 B.M., respectively). Room-temperature solution electronic spectra of precursor and product have one resolved transition between 6000 and 30000 cm^{-1}; the maximum is in each case near 16500 cm^{-1}.

Characterization of the solid-state structure was achieved by an X-ray single-crystal structure analysis. The complex consists of the four-coordinate complex cation and two perchlorate anions. Atom numbering of the complex cation is given in *Fig. 1*, which is an ORTEP plot of the molecular cation. Atomic coordinates, bond lengths, and bond angles are given *Tables 1–3*. Lists of observed and calculated structure factors, H-atom coordinates and thermal parameters, close intermolecular contacts, and details of least-squares planes calculations are deposited as *Supplementary Material*. Each of the perchlorates is disordered over two sites with the Cl-atoms stationary. Both major and minor contributions to the perchlorate O-sites are weakly H-bonded to the amine H-atoms.

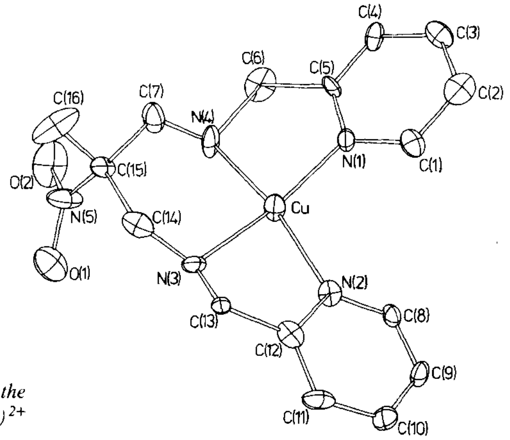


Fig. 1. *An ORTEP plot of the molecular cation* $Cu(ndap)^{2+}$

The geometry around Cu(II) is essentially four-coordinate, though there are weak axial interactions to both major and minor contributions to the perchlorate O-atoms (range 2.70–2.91 Å). The least-squares plane through the Cu- and four-ligating N-atoms reveals a large tetrahedral distortion with the Cu(II) almost in the plane and the N-atoms 0.22–0.25 Å above and below. This distortion is also revealed in the *trans* N–Cu–N angles of 168.0 (7)° and 162.0 (9)°, and results qualitatively in a structure with ~ 80% square planar and ~ 20% tetrahedral character. The ligand forms two five-membered and one six-membered chelate rings. The five-membered rings are slightly puckered [N(1)–C(5)–C(6)–N(4), 10(3)°; N(2)–C(12)–C(13)–N(3), 33(3)°], while the six-membered ring adopts a chair conformation. The pyridine rings are not significantly distorted from planarity but attached Cu- and C-atoms lie up to 0.13 Å out of these planes.

Table 1. *Positional Parameters* ($\times 10^4$) *for* $[Cu(ndap)](ClO_4)_2$

	x	*y*	*z*		*x*	*y*	*z*
Cu(1)	0	4177(1)	7579(2)	N(5)	–741(38)	6797(27)	7985(11)
N(1)	–788(25)	3429(10)	6713(10)	O(1)	–405(20)	6824(11)	8762(11)
N(2)	845(28)	3328(11)	8405(10)	O(2)	–1985(29)	7028(12)	7764(14)
N(3)	1068(21)	5047(12)	8277(9)	Cl(1)	3294(10)	364(5)	1035(5)
N(4)	–1243(23)	5100(11)	7060(13)	O(3)	2452(44)	850(22)	1657(20)
C(1)	–226(47)	2615(27)	6546(14)	O(4)	1988(54)	231(23)	478(22)
C(2)	–805(33)	2142(20)	5870(28)	O(5)	3944(30)	627(26)	289(13)
C(3)	–2054(30)	2482(27)	5413(15)	O(6)	4103(46)	–217(29)	1546(27)
C(4)	–2542(37)	3278(13)	5628(14)	O(3′)	4242(64)	836(46)	1641(30)
C(5)	–1860(38)	3712(11)	6229(12)	O(4′)	3486(35)	–529(29)	1160(28)
C(6)	–2314(23)	4600(28)	6418(28)	O(5′)	1808(10)	534(67)	1102(52)
C(7)	–620(38)	5860(14)	6801(15)	O(6′)	4258(59)	997(37)	744(39)
C(8)	441(37)	2519(11)	8611(12)	Cl(2)	6896(11)	4612(4)	8985(3)
C(9)	1082(25)	2048(13)	9180(14)	O(7)	7352(47)	3954(29)	8421(27)
C(10)	2175(35)	2403(14)	9634(14)	O(8)	6454(31)	5378(26)	8568(15)
C(11)	2664(30)	3260(26)	9475(11)	O(9)	5920(58)	4248(23)	9604(28)
C(12)	2017(24)	3736(29)	8813(14)	O(10)	8331(50)	4836(23)	9409(20)
C(13)	2493(30)	4641(12)	8542(10)	O(7′)	6048(73)	3834(48)	8495(32)
C(14)	1514(20)	5842(27)	7845(12)	O(8′)	8167(88)	4092(44)	8900(49)
C(15)	158(41)	6382(11)	7400(12)	O(9′)	5836(43)	4713(24)	9702(20)
C(16)	975(36)	7045(20)	6867(20)	O(10′)	7733(63)	5464(35)	9093(30)

Table 2. *Bond Lengths* [Å] *for [Cu(ndap)]* $(ClO_4)_2$

N(1)–Cu(1)	1.932(17)	N(2)–Cu(1)	2.002(16)
N(3)–Cu(1)	1.985(17)	N(4)–Cu(1)	1.984(16)
O(7)–Cu(1)	2.778(16)	O(8')–Cu(1)	2.696(17)
O(3)–Cu(1)	2.673(20)	O(5')–Cu(1)	2.914(20)
C(1)–N(1)	1.365(28)	C(5)–N(1)	1.316(27)
C(8)–N(2)	1.325(22)	C(12)–N(2)	1.394(26)
C(13)–N(3)	1.496(27)	C(14)–N(3)	1.450(24)
C(6)–N(4)	1.607(27)	C(7)–N(4)	1.350(26)
C(2)–C(1)	1.403(35)	C(3)–C(2)	1.446(35)
C(4)–C(3)	1.333(27)	C(5)–C(4)	1.322(27)
C(6)–C(5)	1.444(29)	C(15)–C(7)	1.432(31)
C(9)–C(8)	1.296(26)	C(10)–C(9)	1.344(32)
C(11)–C(10)	1.399(27)	C(12)–C(11)	1.413(31)
C(13)–C(12)	1.505(32)	C(15)–C(14)	1.644(33)
C(16)–C(15)	1.515(32)	N(5)–C(15)	1.394(30)
O(1)–N(5)	1.283(21)	O(2)–N(5)	1.235(25)
O(3)–Cl(1)	1.458(34)	O(4)–Cl(1)	1.499(42)
O(5)–Cl(1)	1.392(21)	O(6)–Cl(1)	1.412(27)
O(3')–Cl(1)	1.482(53)	O(4')–Cl(1)	1.385(27)
O(5')–Cl(1)	1.379(93)	O(6')–Cl(1)	1.382(40)
O(7)–Cl(2)	1.410(27)	O(8)–Cl(2)	1.400(24)
O(9)–Cl(2)	1.441(33)	O(10)–Cl(2)	1.509(41)
O(7')–Cl(2)	1.614(55)	O(8')–Cl(2)	1.405(69)
O(9')–Cl(2)	1.508(35)	O(10')–Cl(2)	1.511(53)

Table 3. *Valence Angles* [°] *for [Cu(ndap)]* $(ClO_4)_2$

N(2)–Cu(1)–N(1)	103.8(5)	N(3)–Cu(1)–N(1)	168.0(7)
N(3)–Cu(1)–N(2)	82.5(7)	N(4)–Cu(1)–N(1)	84.5(7)
N(4)–Cu(1)–N(2)	162.0(9)	N(4)–Cu(1)–N(3)	92.5(6)
C(1)–N(1)–Cu(1)	122.4(18)	C(5)–N(1)–Cu(1)	120.3(13)
C(5)–N(1)–C(1)	117.2(19)	C(8)–N(2)–Cu(1)	131.0(14)
C(12)–N(2)–Cu(1)	108.4(16)	C(12)–N(2)–C(8)	120.5(20)
C(13)–N(3)–Cu(1)	108.0(13)	C(14)–N(3)–Cu(1)	115.0(11)
C(14)–N(3)–C(13)	103.7(16)	C(6)–N(4)–Cu(1)	106.2(12)
C(7)–N(4)–Cu(1)	119.6(15)	C(7)–N(4)–C(6)	117.4(18)
C(2)–C(1)–N(1)	118.4(26)	C(3)–C(2)–C(1)	120.1(25)
C(4)–C(3)–C(2)	117.0(24)	C(5)–C(4)–C(3)	119.0(23)
C(4)–C(5)–N(1)	127.8(19)	C(6)–C(5)–N(1)	113.1(18)
C(6)–C(5)–C(4)	119.1(22)	C(5)–C(6)–N(4)	113.8(18)
C(15)–C(7)–N(4)	118.4(20)	C(9)–C(8)–N(2)	124.2(20)
C(10)–C(9)–C(8)	119.4(20)	C(11)–C(10)–C(9)	120.6(22)
C(12)–C(11)–C(10)	118.8(22)	C(11)–C(12)–N(2)	116.2(24)
C(13)–C(12)–N(2)	119.4(21)	C(13)–C(12)–C(11)	124.4(19)
C(12)–C(13)–N(3)	102.1(18)	C(15)–C(14)–N(3)	114.4(17)
C(14)–C(15)–C(7)	112.6(14)	C(16)–C(15)–C(7)	103.5(21)
C(16)–C(15)–C(14)	102.1(24)	N(5)–C(15)–C(7)	114.3(29)
N(5)–C(15)–C(14)	111.9(16)	N(5)–C(15)–C(16)	111.4(18)
O(1)–N(5)–C(15)	121.9(22)	O(2)–N(5)–C(15)	118.2(21)
O(2)–N(5)–O(1)	119.0(22)		

The unit cell symmetry approximates the centrosymmetric space group *Pbcn*. This pseudo-symmetry is conserved by the location of the pyridine ligands and the perchlorate anions, and the Cu-atom lies on a pseudo-two-fold axis. As a consequence of this pseudo-symmetry, refinement of the atoms concerned was difficult and the precision of the final structure limited ($R = 0.068$). All bond lengths and angles are, however, within the expected range.

Electron-spin resonance spectra of the condensed product $Cu(ndap)^{2+}$ and the precursor $Cu(pic)_2^{2+}$ were measured as undiluted powders, and as fluid and frozen solutions in H_2O, DMSO, MeCN, and pyridine, at various temperatures in the range 4 K–300 K. There is only a small solvent dependence of the electron-spin resonance spectra; likewise, electronic spectra show only small variations with solvent, and these observations suggest that axial interactions are weak. The fact that the charge-transfer transitions of $Cu(ndap)^{2+}$ are relatively intense might indicate that there is some interaction of $R–NO_2$ with the Cu^{2+} centre. The rest of the spectroscopic results and the solid-state structure (Cu–O(1) > 4.5 Å) indicate that this interaction is very weak, however. The spin *Hamiltonian* parameters for the complexes are listed in *Table 4*, where data of some published compounds appear for comparison, and typical spectra are shown in *Fig. 2*. The electron spin resonance spectra are consistent with essentially four-coordination and a small tetrahedral distortion from essentially square planar geometry in solution, paralleling the structural observation in the solid state. Detailed analysis is deferred to the *Discussion*.

Table 4. *Spin* Hamiltonian *Parameters and Electronic Transitions for* CuN_4^{2+} *Complexes*

Complex	Elec. spectrum[a]	Spin *Hamiltonian* Parameters[b]						
	$\tilde{\nu}$ (ε)	g_{iso}	$g_{\perp}$	$g_{\parallel}$	A_{iso}	$A_{\perp}$	$A_{\parallel}$	Ref.
$Cu(pic)_2^{2+}$	16790(70)	2.109	2.054	2.220	78	24	194	[c]
$Cu(dap)^{2+}$	16600(143)	2.107[d]	2.053	2.215	69[d]	5	196	[20]
$Cu(ndap)^{2+}$	16560(110)	2.109	2.056	2.216	74	17	196	[c]
$Cu(cyclam)^{2+}$	–	2.099[d]	2.052	2.194	88[d]	29	206	[23]

[a] $\tilde{\nu}$ [cm^{-1}] (ε [M^{-1} cm^{-1}]) in H_2O.
[b] A values in $cm^{-1} \times 10^{-4}$.
[c] This work.
[d] Calculated from cited $g_{\parallel}$, $g_{\perp}$, and $A_{\parallel}$, $A_{\perp}$ values.

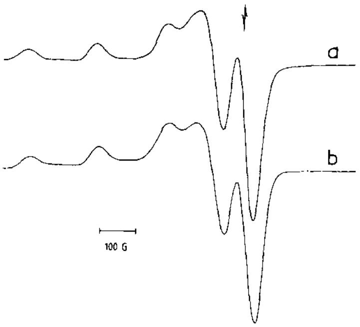


Fig. 2. *Electron spin resonance spectra as frozen solutions in DMSO at 4 K of* (a) $Cu(pic)_2^{2+}$ *and* (b) $Cu(ndap)^{2+}$. The signal for dpph appears at the top of the spectrum.

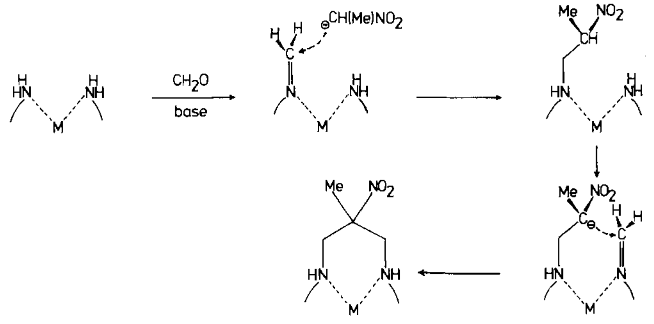
Voltammetry of the condensation product Cu(ndap)$^{2+}$ in aqueous solution (0.5M $NaNO_3$) defined at the hanging Hg drop electrode (HMDE) a quasireversible couple at $E_{1/2} - 0.44$ V *vs.* Ag/AgCl ($\Delta E = 80$ mV, $i_a/i_c = 0.8$, 50 mV/sec). The wave is somewhat complicated by a cathodic adsorption, and is followed by an irreversible multielectron wave with $E_p - 1.06$ V *vs.* Ag/AgCl. Wave-height comparisons with known one-electron couples [10] allowed assignment of the former as a one-electron Cu(II)/Cu(I) couple, and the latter as an irreversible four-electron nitro→hydroxylamine reduction, which is the usual form of this reduction in neutral aqueous solution. The Cu couple ($E° - 0.22$ V) is more negative than the same couple reported for the unsubstituted analogue ($E° - 0.106$ V), while the NO_2-group reduction ($E° - 0.85$ V, from polarography) is of a similar potential to those previously reported for complexed NO_2-substituted amine ligands [10].

Discussion. – Template syntheses of multidentate ligands around a labile metal ion have generally relied on reaction of a dialdehyde or diketone with a complexed multidentate amine, reactions with simple ketones where a base-catalyzed aldol dimerization of the ketone is involved, or, with dithiolates, reaction with dihaloalkanes [11–13]. Other but less general syntheses are known, such as the reaction of Ni(II)-dimethylglyoxime with aminoethyl diphenylborinate to introduce an O–B–O link in the formed multidentate [14]. Formaldehyde alone is known to introduce a CH_2 link between adjacent N-atoms in a labile complex of a dihydrazine ligand [15], but explicit study of reactions of labile amine complexes with formaldehyde and carbon acids has only recently been commenced. The synthesis reported here is the first reaction of the latter type involving ligands with heterocyclic N-donors attached, in which the planarity of the heterocycle results in distortions away from square planarity about the Cu(II) atom in the product.

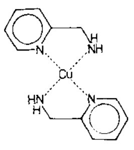
Like the mechanism proposed for synthesis of inert metal-complex analogues [1] [2], the condensation presumably proceeds *via* an imine intermediate, susceptible to attack at the imine C-atom by the conjugate base of the carbon acid (*Scheme*). The formation and relatively high stability of coordinated imines is well documented [16] [17]. The intramolecular path described in the *Scheme* is entropically favoured, and the reaction to the six-membered chelate ring is predestined to be facile and high-yielding. The template reaction reported is, under the conditions described, essentially quantitative.

The solution stereochemistry of the bis(bidentate) precursor complex may be analyzed qualitatively in terms of its spectroscopy and reactivity. The spectroscopy suggests

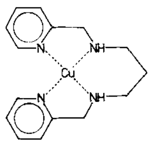
Scheme



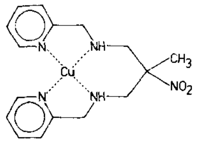
that precursor and product are in solution structurally very similar, *i.e.* tetrahedrally distorted *cis* square planar. However, it has to be noted that increase in covalency in the *xy* plane (such as formation of an additional six-membered chelate ring) and tetrahedral distortion of the chromophore result in opposing trends in terms of the spin *Hamiltonian* parameters, so the spectroscopic similarity of the two species might be accidental. On the basis of reactivity (*i.e.* quantitative formation of the macrocyclic product), one is also driven to suppose *cis*- rather than *trans*-configuration of the precursor complex. However, a tetrahedral distortion together with a reasonable lability of the monosubstituted intermediate could also lead to the observed reactivity. Notably, the bis[2-(2-aminoethyl)pyridine]copper(II) ion, the analogue of our precursor but with six-membered chelate rings, is known to crystallize as the *trans*-isomer from a crystal structure analysis [18]. The different conformational requirements of the six- and five-membered chelate rings may limit the value of this observation as an indicator in this case. Even if the *trans*-geometry of Cu(pic)$_2^{2+}$ is preferred, it is clear that it is the *cis*-isomer which is the reactive species in *Eqn. 3*.



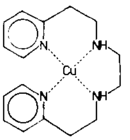
Cu(pic)$_2$



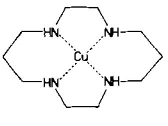
Cu(dap)



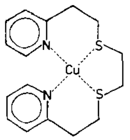
Cu(ndap)



Cu(pdao)



Cu(cyclam)



Cu(pdto)

The unsubstituted parent (dap) of our ligand (ndap) has been prepared previously by another route [19], and its Cu(II) complex is known [20]. The four-coordinate dithioether analogues of diamines like dap have attracted attention because of their value as possible models for blue Cu proteins where two imidazoles, a thioether and a mercaptide bind the copper with distorted tetrahedral geometry. The distortions from planarity observed in the structure of Cu(ndap)$^{2+}$ reported here are similar in nature to those observed in Cu(pdao)$^{2+}$ (pdao = 1,8-bis(2-pyridyl)-3,6-diazaoctane) [21]. These observations suggest that the dithioether analogues may also be distorted and mimic in part the biological geometry. The Cu(II) complex of pdto (1,6-bis(2-pyridyl)-2,5-dithiohexane) reveals no discernable tetrahedral distortion in its crystal structure, although one has to realize that in this case the ion crystallized as the five-coordinate square-based pyramidal Cu(pdto)(ClO$_4$)$^+$ ion with the copper ion above the N_2S_2 plane [22]. At least for the N_4 donors, the enforced planarity of the coordinated pyridine rings affects the geometry about the copper ion, introducing a tetrahedral distortion. In this context, it is important to note that structures of saturated tetraamines about Cu(II) do not show any significant distortions of square planarity; for example, in *trans*-[Cu(cyclam)(SC$_6$F$_5$)$_2$] (cyclam = 1,4,8,11-tetraazacyclotetradecane) the CuN$_4$ chromophore is planar [23].

Both Cu(ndap)$^{2+}$ and Cu(pdao)$^{2+}$ structures show only weak interactions of the ClO_4^- anions in the axial sites, with Cu–O $\geqslant$ 2.70 Å and 2.69 Å, respectively. In solution, interactions in the axial sites appear to be equally weak. *Hathaway* has suggested that square-planar CuN_4 chromophore have d–d transitions in the region of ~ 18000–20000 cm^{-1} [24]. The maximum for Cu(ndap)$^{2+}$ is observed near 16500 cm^{-1}, like the Cu(dap)$^{2+}$ analogue [20], and may imply some weak axial coordination, although one has to realize the limited applicability of such predictions. For both complexes, a slight solvent dependence of the d–d transition frequency and the molar extinction coefficient indicate a weak axial coordination only.

The spin *Hamiltonian* parameters indicate a $(d_{x^2-y^2})^1$ ground state and the g values are compatible with CuN_4 chromophores [25] [26]. However, we note that divergences in g values are quite subtle and may be the result of opposing trends (*e.g.* tetrahedral distortion and increase of covalency), and they are, therefore, not easy to predict. In addition, it was recently pointed out that quantitative information from g parameters can be disappointingly irrelevant [27]. In contrast, A parameters usually give a reasonable indication of the local coordination geometry. For the pyridine ligands, observed values of $A_{\parallel}$ ~ 190G and $A_{\perp}$ ~ 20G are consistent with essentially square planar CuN_4 chromophores, and this supports the electronic spectroscopic evidence that axial interactions are weak. Indeed, the small solvent effects in the electronic spectra and the effect of R–NO_2 on the charge-transfer transition are paralleled by only very small solvent effects in the electron spin resonance spectroscopy.

The absence of any resolved nitrogen hyperfine coupling may be the result of a distortion of the pyridine residues out of the *xy* plane, perhaps arising from a movement of the pyridine rings out of the plane of the five-membered chelates and/or a tetrahedral distortion of the CuN_4 chromophore. We note that a tetrahedral distortion of the CuN_4 plane in solution cannot be large, since any substantial tetrahedral distortion would cause a significant decrease of $A_{\parallel}$ and an increase of $g_{\parallel}$ [28]. All available evidence points, therefore, to a close similarity of solid state and solution structures of Cu(ndap)$^{2+}$ and to similar solution structures of the parent Cu(pic)$_2^{2+}$ and Cu(ndap)$^{2+}$.

The redox chemistry of the Cu(ndap)$^{2+}$ complex is, as expected, similar to that reported previously for Cu(dap)$^{2+}$ [16]. The shift in E° from −0.106 V for Cu(dap)$^{2+}$ to −0.22 V for Cu(ndap)$^{2+}$ is presumably related to the different electronic effects of CH_3 and NO_2 compared with two H atoms on the central C-atom of the six-membered ring. An extensive study of the inductive components of substituent effects on the apical tertiary C-atoms of saturated macrobicyclic hexaamine Co(III) complexes indicated that substituent effects are roughly additive, and that NO_2 and CH_3 substituents shift redox couples in opposite directions relative to hydrogen as standard [14] [10]. No such study has appeared for Cu complexes, particularly where some aromaticity is present in the ligand, so that detailed comment on the small shift is not reasonable here. The observed one-electron couple is not strictly reversible, since cyclic voltammetry on both glassy C and Pt working electrodes show that the return anodic wave is less well defined than is the case at the Hg electrode, and the process is irreversible on the coulometric timescale in aqueous solution. For the Cu(dap)$^{2+}$ analogue in MeCN, the couple has been defined as a one-electron couple from coulometry [20], and wave-height comparisons with known reference complexes define a one-electron couple for Cu(ndap)$^{2+}$ in this study.

Extension of the type of synthetic reaction described here to other precursors and investigation of the structural and spectroscopic properties and reactivities of their products is being pursued.

Experimental. – *Syntheses. Bis[2-(aminomethyl)pyridine]copper(II) Perchlorate.* To a suspension of $Cu(NO_3)_2 \cdot 3\ H_2O$ (1.0 g) in MeOH (100 ml) was added 2-aminomethylpyridine (0.9 g) while stirring. Addition of sat. aq. $NaClO_4$ soln. (20 ml) and cooling produced light purple crystals which were collected, washed with MeOH and air-dried (1.8 g, 90%). Electronic spectrum (H_2O; λ_{max} [nm] (ε [M^{-1} cm^{-1}]): 596 (70), 252 (8750), 235 sh (8300). Anal. calc. for $C_{12}H_{16}Cl_2CuN_4O_8$: C 30.11, H 3.37, N 11.70, Cu 13.28; found: C 30.4, H 3.3, N 11.6, Cu 13.4.

[N,N'-Bis(2-pyridylmethylene)-1,3-diamino-2-nitropropane]copper(II) Perchlorate. A mixture of $Cu(NO_3)_2 \cdot 3\ H_2O$ (5.0 g), 2-aminomethylpyridine (4.4 g), nitroethane (1.75 g) and 37% aq. formaldehyde soln. (5.0 g) in MeOH (750 ml) was stirred and warmed to ~ 50°, with ethanolamine (0.5 ml) added as base. After 4 h, the suspension was treated with excess nitroethane (~ 10 ml), 37% aq. formaldehyde soln. (~ 25 ml) and H_2O (~ 350 ml), and stirring and heating continued for 2 h. The soln. was filtered, and the volume reduced to ~ 0.5 l on a rotary evaporator. Sat. aq. $NaClO_4$ soln. (~ 100 ml) was added slowly with stirring at r.t. A dark blue-purple crystalline precipitate formed and was collected, washed with ice-cold H_2O (20 ml), then with MeOH and Et_2O, and air-dried (9.8 g, 85%). IR (KBr): $\tilde{\nu}_{as}$ (NO_2), 1555; $\tilde{\nu}_s$ (NO_2), 1355. Electronic spectrum (H_2O): 604 (110), 254 (12, 400). Anal. calc. for $C_{16}H_{21}Cl_2CuN_5O_{10}$: C 33.26, H 3.66, N 12.12, Cu 11.00; found: C 33.5, H 3.7, N 11.9, Cu 11.05.

Physical Methods. IR spectra were recorded as KBr discs using a *Perkin-Elmer 3-300* spectrometer. Electronic spectra were recorded on *Hitachi 220A* and *Cary 17* spectrophotometers. Electron spin resonance spectra were recorded on a *JEOL JES-PE* spectrometer fitted with an *Oxford Instruments ESR 9* He flow cryostat and a *Model DTC 2* temp. controller, or on a *Brunker ER 200D-SRC* spectrometer. Concentrations of the fluid or frozen solns. were in the range 10^{-5} to 10^{-3} M, while powders were undiluted. Magnetic moments were measured at ambient temperature, by the *Guoy* method. Voltammetry was performed at HMDE, DME, or at glassy C or Pt billet working electrodes, with potential measured *vs.* Ag/AgCl. A conventional three-electrode system and *BAS Model CV27* or electrochemical controllers were employed, with Ar as purge gas.

X-Ray Crystal-Structure Determination. Crystal Data: $C_{16}H_{21}Cl_2CuN_5O_{10}$, M_r 577.82, orthorhombic, space group $P2_1cn$, $a = 9.083(2)$, $b = 15.198(3)$, $c = 16.025(3)$, $U = 221.2$ Å^3, $Z = 4$, $D_c = 1.735$ g cm^{-3}, $\mu(MoK\alpha) = 12.45$ cm^{-1}, $\lambda(MoK\alpha) = 0.7107$ Å, $F(000) = 1180$ electrons. Lattice parameters were determined by a least-squares fit to the setting angles of 25 independent reflections in the range $15 < 2\theta < 25$. Intensity data were collected using an *Enraf-Nonius CAD4F* four-circle diffractometer in the range $1.0 < \theta < 25.0°$ using a ω-$\theta/3$ scan. The ω scan angles and horizontal counter apertures employed were $(1.40 + 0.35 \tan\theta)°$ and $(2.40 + 0.50 \tan\theta)$ mm, resp. Data reduction was performed using program SUSCAD [29] and absorption corrected for using program ABSORB [29] (maximum and minimum corrections 1.19 and 1.08). Of the 2243 reflections collected, 1175 unique reflections with $I > 2.5\sigma(I)$ were used in the calculations. The structure was solved by heavy-atom methods and refined by successive application of least-squares refinement and difference *Fourier* methods. H-atoms were included at calculated sites (C–H 0.97 Å, N–H 0.91 Å) with group thermal parameters. All non-H-atoms were modelled anisotropically. All parameters and an overall scale factor were refined by full-matrix least-squares methods using SHELX-76 [30]. Refinement converged with $R = 0.068$, $R_w = 0.071$, $w = 3.65/(\sigma^2(F_o) + 0.00036\ F_o^2)$. Maximum and minimum excursions in a final difference map were +0.5 and −0.5 eÅ^{-3}, resp. Scattering factors (neutral Cu for Cu(II)) and anomalous dispersion terms were taken from the *International Tables for X-Ray Crystallography* [31].

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