Copper Complexes of some Tetradentate Pyrazolyl Amines

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Abstract

Four tetradentate nitrogen donor ligands have been prepared by condensation of *N*-hydroxymethylpyrazoles with ethylenediamines. These ligands are varied by methylation of the pyrazole rings (edbd) or the aminonitrogens (debp), or both (debd). Copper(II) complexes of the type $CuL(ClO_4)_2$ have been isolated with L = debp, edbp, edbd. For L = debd, the adducts salts $Cu(debd)(dMp)X_2$, with $X = ClO_4^-$, BF_4^- and dMp = 3,5-dimethylpyrazole, were obtained. The compounds were characterized by their absorption (d–d) and EPR spectra. All four undergo quasi-reversible electrochemical reduction in methanol, the redox potentials being correlated with the degree of ligand methylation. The copper(I) forms are relatively unstable, and also bind carbon monoxide with different affinities.

Introduction

The redox chemistry of copper continues to attract considerable attention [1], as the most marked property of copper ions in biochemistry is their ability to change oxidation state [2]. The electrochemical properties of the copper ion are controlled by the ligands' donor atoms and the coordination geometry. For type-1, or 'blue', copper proteins, this results in rapid electron transfer kinetics and relatively high redox potentials. Compounds with a variety of donor atoms and steric constraints have been studied [1–8], in order to elucidate structure–redox relationships.

As histidine-imidazole mimics, the heterocyclic nitrogen-donor pyrazole-derived ligands 1,6-bis(pyrazolyl-1-yl)-2,6-diazahexane (edbp), 1,6-bis(pyrazol-1-yl)-2,5-dimethyl-2,5-diazahexane (debp) and the 3,5-dimethylpyrazol-1-yl analogues, edbd and debd respectively, provide a series of ligands with very similar donor groups in a conformation allowing chelation (see Fig. 1).

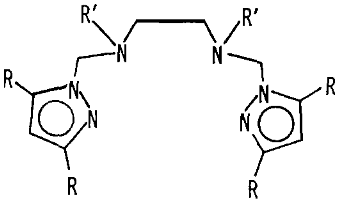

Fig. 1. Structural formula of the ligands: R'–H, R = H, edbp; R' = H, R = Me, edbd; R' = Me, R = H, debp; R' = Me, R = Me, debd.

The steric influence of the methyl groups on the pyrazole rings in debd has been established as hindering the coordination of larger-donor atom ligands like bromide [9–11]. The influence of the steric properties of the methyl groups in pyrazolylborate ligands in the electrochemical properties of molybdenum compounds has been investigated [7]. The methyl groups, particularly on the pyrazole rings in debd and edbd, are expected to have steric influence as well as electronic effects.

We present here the synthesis of $Cu(ClO_4)_2$ compounds with the four ligands and one tetrafluoroborate compound together with their spectroscopic and electrochemical properties.

Experimental

Most solvents, metal salts and starting reagents were commercially available and used without further purification. Argon and carbon monoxide were supplied by Burdett/MG Industrial Gases Ltd. Methanol (MeOH) for electrochemistry was spectrophotometric grade, or was distilled off magnesium turnings under dinitrogen. G. F. Smith tetrakis(n-hexyl)ammonium perchlorate (THAP) was recrystallized from aqueous MeOH and dried in vacuum over P_4O_{10}.

The ligands debd and debp have been reported previously [9, 11]; edbp and edbd were synthesized

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from the 2-hydroxymethylpyrazoles and 1,2-diaminoethane by the same procedure, using stoichiometric ratios in aqueous solution (3 l per mole of pyrazole). After five days, the products were extracted with dichloromethane, evaporation of which solvent yielded the desired ligand as a white solid (edbp), or as a clear, colorless oil (edbd). Characterization by ^{1}H NMR (δ ppm *versus* TMS): edbp = 6.24 (2H; C_4); 7.65, 7.44 (4H; C_3, C_5); 4.92 (4H; $-CH_2$); 2.79 (4H; $-CH_2-CH_2-$); edbd = 5.72 (2H; C_4); 4.71 (4H; $-CH_2$); 2.79 (4H; $-CH_2-CH_2-$); 2.20, 2.10 (12H; $-CH_3$).

The complexes were prepared by addition of hydrated copper(II) perchlorate or tetrafluoroborate (5 mmol) in warm ethanol (15 ml) to a solution of the ligand (5 mmol) in 15 ml ethanol. The copper(II) debd-tetrafluoroborate crystallized from the cooled solution. The debd, edbp and edbd perchlorates separated as colored oils, which solidified upon standing, while the debp-perchlorate was obtained by allowing the solution to stand for several days below −10 °C. The solid products were filtered off, washed extensively with diethyl ether, and dried.

Caution. The potentially explosive perchlorates should be handled with great care.

Anal. Found (calc.)

$Cu(edbp)(ClO_4)_2 = C_{10}H_{16}Cl_2CuN_6O_8$ (deep blue powder): C, 26.91 (24.88); H, 3.45 (3.34); N, 18.9 (17.4); Cl, 14.4 (14.7); Cu, 13.5 (13.2); remainder, 22.8; (O (26.5)).

$Cu(debp)(ClO_4)_2 = (C_{12}H_{20}Cl_2CuN_6O_8$ (deep blue crystals): C, 28.22 (28.22); H, 3.95 (3.95); N, 16.7 (16.5); Cl, 14.2 (13.9); Cu, 12.9 (12.4); remainder, 24.0; (O (25.1)).

$Cu(edbd)(ClO_4)_2 = C_{14}H_{24}Cl_2CuN_6O_8$ (bright blue powder): C, 33.71 (31.21); H, 4.84 (4.49); N, 16.2 (15.6); Cl, 12.7 (13.2) Cu, 12.2 (11.8); remainder; 20.4 (O (23.8)).

$Cu(debd)(dMp)(ClO_4)_2 \cdot H_2O = C_{21}H_{39}Cl_2CuN_8O_9$ (bright blue powder): C, 36.42 (36.98); H, 5.28 (5.76); N, 16.9 (16.4); Cl, 10.8 (10.4); Cu, 9.35 (9.32); remainder; 21.3 (O (21.1)).

$Cu(debd)(dMp)(BF_4)_2 \cdot H_2O = C_{21}H_{39}B_2CuF_8N_8O$ (bright blue crystals): C, 38.4 (38.40); H, 5.83 (5.99); N, 16.9 (17.1); F, 22.4 (23.1); remainder 16.5; (B (3.29), Cu (9.67), O (2.44)).

Infrared spectra (4000–180 cm^{-1}) were recorded on a Perkin-Elmer PE 380 instrument, using KBr pellets and/or nujol mulls between NaCl or polyethene discs.

Electronic spectra (2000–300 nm) were measured on a Perkin-Elmer UV330 instrument, equipped in the diffuse reflectance mode with MgO as a reference. EPR spectra were obtained on a Varian E-3 X-band spectrometer. Proton NMR spectra (in dmso-d_6 solutions) were recorded in the CW mode on an externally locked JEOL LNM PS100 instrument, operating at 99.5 MHz with TMS as an internal reference. FT NMR spectra were recorded on a JEOL JEC 980B instrument, operating at 199.5 MHz (^{1}H), using ^{2}H as an internal lock. TMS or the dmso-d_6 resonance 2.450 ppm downfield was used as a reference.

Elemental analyses were performed by the Microanalytical Laboratory of University College, Dublin, and Canadian Microanalytical Service Ltd. Conductivity measurements were performed on 1 mM solutions in nitromethane, using a Seibold LTB conductometer.

Electrochemical measurements were made on 0.5–2.0 mM solutions of complex in MeOH/THAP at 25.0(±0.2) °C under an argon atmosphere, using a three-electrode configuration. Potentials were measured with respect to an Ag/Ag^+ (0.01 M, 0.1 M NEt_4ClO_4, CH_3CN) reference electrode and may be expressed with reference to the standard hydrogen electrode by the addition of +544 mV. A 0.282 cm^2 platinum sphere electrode, used as the stationary working electrode for cyclic voltammetry, was cleaned by successive treatments with dilute nitric acid and hydrazine and rinsed with water and methanol. A Beckman rotating platinum disc (RPE, area 0.300 cm^2) was used for rotating electrode polarography, and was cleaned by abrasion. A PAR-173/176/178 potentiostat system was used in conjunction with an X–Y recorder and a Nicolet digital oscilloscope.

Viscosity and density values for the MeOH/THAP solutions were determined (Ubbelohde viscometer) at 25 °C to be 0.00651 ± 0.00003 g cm^{-1} s^{-1} and 0.791 g ml^{-1} respectively.

Results and Discussion

General

The analytical results for $Cu(debp)(ClO_4)_2$ are in agreement with the proposed molecular formula. The analyses of the edbd and edbp compounds indicate the presence of small amounts of copper(I) arising from autoreduction of the complexes during synthesis, as revealed by the low content of chlorine, consistent with the excess of C, H and N, and particularly the low ratio Cl/Cu. Spectroscopic data do not indicate the presence of other copper(II) species besides the desired compounds. No attempts were undertaken to maximize the Cu(II) content of the compounds, because of the ease of autoreduction. In contrast, the analytical data for the debd complexes clearly show that the compounds contain an additional 3,5-dimethylpyrazole (dMp) molecule, which presumably is coordinated to the copper.

Spectroscopic Properties

The infrared spectra of the compounds all show the presence of perchlorate anions, with vibrations

TABLE I. Spectroscopic Properties of $Cu(L)(ClO_4)_2$ Compounds

		Ligand			
		debd	edbd	debp	edbp
$g_\parallel$	(solid, 293 K)	2.24	2.24	a	b
$10^4 \times A_\parallel$ (cm^{-1})	(solid, 293 K)	180	170	a	b
$g_\perp$	(solid, 293 K)	2.07	2.07	2.07	2.08
g_0	(MeOH, 297 K)	2.129	2.126	2.119	2.114
$10^4 \times A_\parallel$ (cm^{-1})	(MeOH, 297 K)	71	63	63	72
$g_\parallel$	(MeOH, 77 K)	2.240	2.235	2.288	2.28
$10^4 \times A_\parallel$ (cm^{-1})	(MeOH, 77 K)	190	183	160	160
$g_\perp$	(MeOH, 77 K)	2.05	2.06	2.08	2.08
$(g_\parallel - 2)/A_\parallel$	solid	13.3	14.1		
$(g_\parallel - 2)/A_\parallel$	(MeOH, 77 K)	12.6	14.1	18.0	17.5
g_{av}/solid		2.13	2.13		
g_{av}/77 K		2.11	2.12	2.15	2.15
$10^3 \times \nu_{max}$ (cm^{-1})	(solid, 293 K)	15.8	16.8	16.4	17.0
$10^3 \times \nu_{max}$ (cm^{-1})	(MeOH, 293 K)	15.2	15.2	15.6	16.2
ϵ (M^{-1} cm^{-1})		176	121	104	102

[a]Not resolved. [b]Not sufficiently resolved.

at 600 cm^{-1} and around 1100 cm^{-1}. The vibrations are unsplit, so that no anion coordination is evident. The non-coordinating nature of the anions is also exemplified by the conductance value of the compound $Cu(debd)(dMp)(ClO_4)_2 \cdot H_2O$ (158 S mol^{-1} cm^2 for a 1 mM solution in CH_3NO_2, in agreement with the value expected for a 1:2 electrolyte [12]). Characteristic ligand vibrations are also observed, and infrared spectra of samples from different batches are identical.

Relevant EPR data and ligand field spectroscopic data are given in Table I. The data are indicative [13] of tetragonal symmetry. As there is no indication of strong perchlorate coordination in the solid state, it is presumed that essentially tetracoordination is indicated, except, of course, for the dMp adduct of the debd complexes: The relative constancy of the spectroscopic parameters for the copper debd perchlorate compound shows that the copper coordination is essentially the same in solution at both 77 and 297 K as it is in the solid state. Prior crystallographic studies [9–11] indicate that debd is unlikely to adopt a square-planar coordination, so a somewhat distorted CuN_5 chromophore for it in the solid state is presumed. The higher ratios of $(g_\parallel - 2)/A_\parallel$ [2, 14] for the debp and edbp complexes support the idea of some pseudotetrahedral distortion in cryogenic MeOH solution for the complexes with non-methylated pyrazoles. Comparison of these EPR cryogenic spectra with their solid state spectra does not show any marked differences apart from better resolution of the $g_\parallel$ region in the methanol glasses. The absence of any rhombic features [14] in the EPR spectra, which one would expect by analogy with $Cu(dedb)(NCS)_2$ [15], is not inconsistent though, with solvation in the *xy* plane in MeOH. It can thus be concluded that the non-methylated pyrazole complexes probably retain the distorted geometry of their CuN_4 moieties on dissolution in methanol. Such distortions are well known as consequences of steric hindrance [16, 17]. A lesser effect is noted from *N,N'*-dimethylation of edbp.

Comparison of the EPR data for the various compounds shows that pyrazole methylation decreases $g_\parallel$ and increases $A_\parallel$, so that $(g_\parallel - 2)/A_\parallel$ is decreased. This is indeed consistent with the inductive properties of methyl substituents [18], but this interpretation is vitiated by their observed influence (*vide infra*) on the redox potentials. The alternative interpretation, that the principle (*xy*) plane of the pyrazole-methylated complexes in solution is now a flattened CuN_3O chromophore, is supported by the longer-wavelength d–d band of the edbd (and the axial N-ligated debd) complex, consistent with the consequently increased axial donor strength [19].

Electrochemical Properties

Cyclic voltammetry at a stationary platinum sphere electrode and rotating platinum electrode polarography were employed to investigate the

TABLE II. Electrochemical data for $Cu(L)(ClO_4)_2$ Compounds

Ligand	$E_{1/2}$ (V)[a]	ΔE_p (mV)[b]	$10^6 \times D$ ($cm^2\ s^{-1}$)[c]
edbp	−0.21 +0.23[d]	133	3.9
debp	−0.13 +0.22[d]	100	5.2
edbd	−0.18 +0.29[d]	103	3.4
debd	−0.08 +0.20[d,e]	106	2.3

[a] Referred to nonaqueous electrode: add 0.544 V for SHE as reference. [b] At scan rate 0.05 V s^{-1}. [c] From RPE polarogram. [d] Additional anodic peak. [e] Weak current peak.

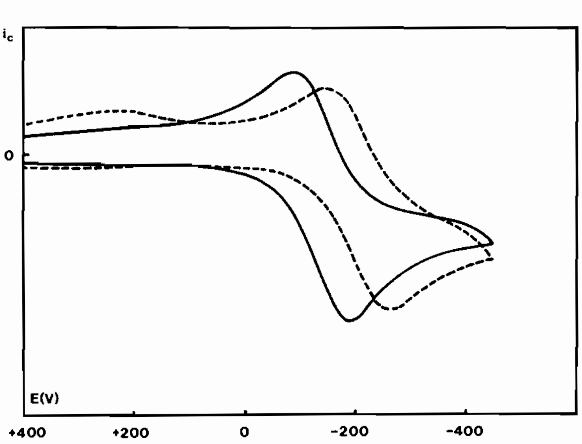

Fig. 2. Cyclic voltammetry of $Cu(edbp)(ClO_4)_2$ in MeOH/THAP at 25 °C in the absence (broken trace) and presence (solid trace) of carbon monoxide. Scan rate = 0.05 V/s.

electrochemical behaviour of the pyrazolyl complexes in methanol. The $E_{1/2}$ values of the Cu(II)/Cu(I) couples, as well as the peak potential separations, ΔE_p from the cyclic voltammograms obtained at 0.010 V s^{-1} are collected in Table II. The diffusion coefficients were estimated from the limiting (plateau) currents of the RPE polarograms using the Levich equation [20]

$$i_{\text{lim}}\ (\mu A) = 9.48 \times 10^5\ nA(D)^{2/3}C(\omega)^{1/2}(\nu)^{-1/6}$$

where C is the concentration (mM) of the copper compound, ω the electrode rotation rate and ν the kinematic viscosity (in $cm^2\ s^{-1}$).

Not only are the shapes of the cyclic voltammograms consistent with $n = 1$ (see Fig. 2), $Cu^{2+} + e^- \leftrightharpoons Cu^+$ processes, but also the $D(\eta)$ values from the RPE polarography lie in a range ($2.8 \pm 0.5 \times 10^{-8}$ g cm s^{-2}) appropriate for $n = 1$ rather than $n = 2$ processes [14].

For a Nernstian one-electron redox system at the spherical electrode used here, we expect [21] to observe $\Delta E_p = E_{p,a} - E_{p,c}$ of about 65 mV (uncompensated iR-drop also adds *ca.* 10 mV at scan rate $\nu = 0.1$ V s^{-1}). The values observed for these complexes, ranging from 100 to 133 mV at $\nu = 0.05$ V s^{-1} and increasing with increasing scan rate, indicate that they are not diffusion-controlled, but quasi-reversible redox processes. At all scan rates the ΔE_p values are dependent on the methyl substitution; the order of reversibility, based on this criterion, decreases as (R_1, R_2) Me,H > Me,Me > H, Me > H,H, so that N-methylation is not only effective in raising the $E_{1/2}$, but also in conferring reversibility on the system.

We propose two causes for the non-Nernstian ΔE_p values and their marked dependence on scan rate: (i) the electron-transfer is likely limited by heterogeneous electron transfer kinetics at the Pt electrode, and (ii) there is a coupled homogeneous chemical reaction process. The latter (which interferes with the extraction of any electron-transfer rate constants from the data) is clearly evidenced by the occurrence, in all the compounds' cyclic voltammograms, of a second anodic current peak (i_{a2}), about 0.4 V more positive than the primary one. There is no anomalous cathodic current behaviour, and the secondary anodic peak is least discernible in the debd complex. This suggests an EC mechanism, the homogeneous reaction step of which is connected to other observations regarding the compounds: (i) attempts to synthesize simple copper(I) complexes of the type $Cu(L)ClO_4$ gave very low (<5%) yields, due to apparent metal-induced decomposition of the ligand in the MeOH/MeCN/Cu(I) system used; Indeed, for debd, this is manifested by the formation of the dMp adduct. (ii) The secondary, more positive anodic peak disappears when the solutions are saturated with carbon monoxide.

Though less significant for the debd complex, the effect of CO is quite apparent for the other three chelates, being most pronounced for the copper–edbp system. In this last case, the principal cathodic and anodic current peaks are also both shifted anodically by 64 mV, indicating preferential binding of CO by copper(I), with an equilibrium constant [19] value of *ca.* 11 atm^{-1} at 25 °C.

The results indicate that CO-binding correlates inversely with the degree of ligand methylation; for debp, the potential shift is quite small (*ca.* +12 mV) and appears only on the anodic peak, while the latter is also true for $Cu(edbd)^+$ (+50 mV). Therefore, in at least these latter two instances, any CO-binding is kinetically coupled to the redox process in the voltammetry timescale used.

A simple minimal scheme which is consistent with the synthetical and electrochemical observations is:

$$\begin{tikzcd} CuL^{2+} + e^- \arrow[r, shift left, "E"] & CuL^+ \arrow[l, shift left] \arrow[r, shift left, "C"] \arrow[d, shift left, "\pm CO"] & CuX^+ \arrow[l, shift left] \\ & Cu(L)(CO)^+ \arrow[u, shift left] & \end{tikzcd}$$

L represents the N_4-chelating agent, while the +0.2 V oxidation wave is associated with oxidation of the reaction product CuX^+, which is likely the consequence of the same processes which foil the CuL^+ syntheses. As $i_{p,a}/i_{p,c}$ increases only slightly with scan rate, and $i_{a2}/i_{p,c}$ increases by only 8% with a tenfold increase in ν, the homogeneous reaction process is more likely an equilibrium than an irreversible reaction on the voltammetric timescale. The new copper(I) species CuX^+ appear at more positive redox potentials, *i.e.* they are more stable relative to their copper(II) counterparts than are the original compounds.

Attempts to isolate $CuL(CO)ClO_4$ were also unsuccessful; in view of the weak and often non-equilibrium CO-binding, it is not surprising that the process 'C' is retarded sufficiently that little net reaction is observed on the voltammetric timescale, but that the pathway is still consequential enough to interfere with syntheses.

It has been suggested previously [22] that the redox potentials can be considered to be additive and apportioned into contributions from ligand factors like alkyl substitution, chelate ring effects, number and types of donor atoms etc. In the present compounds a certain regularity is indeed observed in the $E_{1/2}$ values; each N-methylation elevates $E_{1/2}$ by 45 ± 5 mV, while each pyrazole dimethylation elevates it by 20 ± 5 mV. The higher redox potential is indicative of a stabilization of the copper(I) state relative to the copper(II) state. The electron-donating (inductive) properties of the various methyl substituents cannot be invoked to account for these trends in redox potential, as they should thus preferentially stabilize copper(II) [23]. The effects of ligand methylation on the redox potentials must therefore derive from their structural and geometric consequences, rather than their inductive properties. For four-coordinate copper complexes, increasing tetrahedral distortion is associated with more positive redox potentials [16], and the same type of criterion has been applied to pentacoordinate copper(II) systems as well [24], and it seems equally likely, that increasing methylation in the present systems may more significantly result in weaker solvation of, and consequent destabilization of copper(II). Indeed, decreasing tendency for carbon monoxide to interact with the copper(I) complexes is also correlated with increasing ligand methylation.

Conclusion

Four pyrazole-containing ligands have been synthesized starting from the ethylenediamine unit. The properties of the copper(II) perchlorate chelates, obtained with these ligands, are affected by the presence or absence of methyl groups on the pyrazole rings and the amine nitrogens. The electrochemical properties are significantly influenced by the resulting structural differences. The stronger influence is exerted by steric effects caused by methylation of the amine nitrogen. Methylation not only affects the redox potential and the reversibility of the redox process, but also inhibits interaction of small molecule ligands with the metal in both its oxidation states.

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