3.3. Réduction de Ni\(^{2+}\) en présence de complexants

La réduction électrochimique de Ni\(^{2+}\) complexé par divers acides carboxyliques a été étudiée dans une cellule à cathode volumique de type PU 20 ppi. L’aire cathodique totale était de 0,26 m\(^2\) pour un volume de réacteur de 1,9 \(10^{-3}\) m\(^3\), ce qui correspond à un rapport aire cathodique/volume du réacteur de 140 m\(^{-1}\). L’électrolyte est une solution 0,1 M de Na\(_2\)SO\(_4\) à pH 6, contenant environ 100 ppm de Ni\(^{2+}\) et 1% de divers acides carboxyliques. La vitesse linéaire de l’électrolyte percolant les électrodes est de 8 \(10^{-3}\) m s\(^{-1}\). Une bonne agitation est assurée par de l’air introduit en bas de la cellule. Les résultats obtenus sont présentés sur la fig 7. On constate qu’en prolongeant la durée de la réduction, on peut atteindre une concentration en Ni\(^{2+}\) inférieure à 2 ppm en présence de tous les acides testés, à l’exception de l’acide citrique. La spéciation du Ni en présence d’acide citrique est actuellement étudiée par polarographie et au moyen d’une électrode spécifique.

Une partie de ce travail a été subventionnée par la Commission pour l’encouragement de la recherche scientifique (crédit CERS No. 1762.1).

Reçu le 20 janvier 1992

[1] Nomenclature: \(I_\text{K}\): courant limite \([A]\), \(n\): nombre d’électrons échangés, \(F\): constante de Faraday \([A \cdot s^{-1}\cdot \text{mol}^{-1}]\), \(A\): aire de l’électrode \([m^2]\), \(K_\text{v}\): coefficient de transfert de matière \([m^s^{-1}\cdot \text{mol}^{-1}]\), \(C_{\text{D}}\): concentration de l’espèce électroactive dans l’électrolyte \([\text{mol} \cdot m^{-3}]\), \(A\): aire spécifique par unité de volume \([m^2 \cdot m^{-3}]\) ou \(m^{-1}\), \(v\): vitesse moyenne de l’électrolyte \([m^s^{-1}]\), \(L\): longueur de l’électrode volumique dans le sens du flux \([m]\), \(Q\): débit volumique de l’électrolyte \([m^s^{-1}]\), \(S\): nombre adimensionnel de Sherwood.

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Abstract. The flexible bidentate ligand \(1,3\)-bis(benzimidazol-2-yl)propane, \(L^3\), and its \(N\)-methylated derivative \(L^4\), form complexes with Cu\(^{I}\) and Cu\(^{II}\). The X-ray crystal structure of \([\text{Cu}(L^4)(\text{MeCN})](\text{PF}_6)\) (1) shows a trigonal coordination of the Cu\(^{II}\) with the eight-membered chelate ring adopting a half-chair conformation. With Cu\(^{II}\) in EtOH, \(L^3\) forms dimeric \([L^3\text{Cu}(\mu-\text{EtO})\text{Cu}(L^3)]\text{ClO}_4\cdot 2\text{EtOH}\) (2) whose X-ray crystal structure shows Cu\(^{II}\) in a distorted square-planar environment with one bidentate ligand and two bridging ethoxides. The chelate ring now has a boat-chair conformation which forms a hydrophobic pocket around the metal.

Introduction

The formation of polynuclear complexes with unusual structural features such as double helices \([1]\), triple helices \([2]\), or knots \([3]\) is a subject of current interest in coordination chemistry. Some years ago \([4]\), we showed that the ligand 2,6-bis(1-methylbenzimidazol-2-yl)pyridine, \(L^1\), forms with Cu\(^{I}\) a double helical-dinuclear complex \([\text{Cu}(L^1)_2]^{2+}\), in which \(L^1\) acts as a bis-monodentate ligand, wrapping around the Cu–Cu axis in such a way as to give a linear coordination of the Cu–atom. The complex shows a weak bridging interaction due to the pyridines, and a strong stacking interaction between benzimidazoles in the two strands. If the pyridine of \(L^1\) is replaced by a Ph group to give 1,3-bis(1-methylbenzimidazol-2-yl)benzene, \(L^2\), reaction with Cu\(^{I}\) also affords a dinuclear complex \([\text{Cu}(L^2)_2]^{2+}\) \([5]\), in which the Cu-atom is still linearly coordinated, but the complex is now centrosymmetric, with the ligand adopting a different conformation in which a stacking interaction between the bridging Ph groups is possible. \([\text{Cu}(L^3)_2]^{2+}\) may be regarded as a conformer of \([\text{Cu}(L^1)_2]^{2+}\), since the two structures may be interconverted simply by twisting about Cu–N and benzimidazole–Ph or benzimidazole–pyridine bonds. The double-helical structure of \([\text{Cu}(L^1)_2]^{2+}\) is not possible for \([\text{Cu}(L^2)_2]^{2+}\), since it would result in unacceptably short Cu–H distances; it was, therefore, of interest to study the more flexible ligand 1,3-bis(benzimidazol-2-yl)propane, \(L^3\), and its \(N\)-methylated derivative \(L^4\), which maintain the three C–atom spacer between the benzimidazoles, but give two additional torsional angles of freedom. In this paper, we present the X-ray crystal structures of complexes of \(L^3\) and \(L^4\) with Cu\(^{II}\) and Cu\(^{I}\), respectively.

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Results

Synthesis. The ligand L3 is obtained in good yield from 1,3-propane-dicarboxylic acid and 1,2 diamino- benzene using a modified Phillips reaction [6], and may readily be methylated to give L4 [5]. L4 was used for reactions with Cu to avoid oxidation catalyzed by the slightly acidic imidazole protons of complexes of L3. The colorless complex [Cu(L4)(MeCN)](PF6), 1, was obtained by treatment of [Cu(MeCN)4](PF6) in acetonitrile solution with a solution of L4 in CH2Cl2. Reaction of L3 with copper(II) perchlorate in ethanol afforded low yields (typically 30%) of [(L3)Cu(μ-EtO)2Cu(L3)](ClO4)2.

Fig. 1. ORTEP [14] views of [Cu(L3)(MeCN)]+. a) Approximately perpendicular to the ligand plane. Bond distances Cu–N(1) 1.960(7), Cu–N(3) 1.977(5), Cu–N(O1) 1.912(9) Å; bond angles N(1)–Cu–N(3) 118.1(3)°, N(1)–Cu–N(O1) 121.6(3)°, N(3)–Cu–N(O1) 120.0(3)°. b) View approximately along the pseudo-twofold axis, showing the half-chair conformation of the chelate ring (thick bonds).
2EtOH, 2, as a brown solid which could be recrystallized from MeCN/EtOH.

**Structure of 
[(L^4)Cu(MeCN)]PF_6 (1).**

The structure of the cation 
[(L^4)Cu(MeCN)]^+ Fig. 1, shows that L^4 does not form a dinuclear Cu complex as do L^1 and L^2, presumably since the flexibility of the ligand allows the formation of the entropically more favorable mononuclear complex. The coordination geometry of the Cu-atom is almost ideal trigonal with a bite angle for the chelate ligand of 118.1(3)°. Bond lengths and angles show no features of particular interest. The eight-membered chelate ring has a half-chair conformation with a non-crystallographic two-fold symmetry axis passing through the Cu-atom and the central atom of the propane bridge (ΔC_2 = 0.019(2) [7]). The Cu-atom lies in the mean plane of the ligand [8], and the total puckering amplitude Q_T = 1.256(8) Å. The benzimidazoles occupy quasi-equatorial positions with an angle of 145.9(2)° between their least-squares planes. The crystal packing shows alternate layers of cations and PF_6^- anions, with stacking interactions between benzimidazoles of different cations located on either side of a centre of symmetry (inter-plane distance 3.55 Å).

**Structure of 
[(L^4)Cu(μ-EtO)₂Cu(L^3)] (ClO_4)_2 · 2EtOH (2).** The formation of a brown crystalline product from the green solution of L^3 and Cu^II, albeit in low yield, was surprising, and prompted the determination of the crystal structure of this compound, which was revealed to be a di-μ-EtO dimer (Fig. 2), with a centre of symmetry between the two Cu-atoms. The coordination of the Cu-atom is distorted square-planar, with two bridging EtO anions and a Cu-Cu' distance of 2.979(2) Å. The Cu-N bond distances are identical within experimental error to those observed for 1, but the bite angle of the chelate ligand is 88.5(3)°, 30° less than that observed in 1. This decrease results in a change in chelate ring conformation (Fig. 3), the eight-membered ring now adopting a stable boat-chair conformation [9] with the Cu-atom as the prow of the boat. There is a non-crystallographic mirror plane (ΔC_2 = 0.020(2) [7]) passing through the Cu-atom and the central atom of the propane bridge. The Cu-atom is now the atom which shows the greatest deviation (0.948(4) Å) from the mean plane of the chelate ring although the total puckering amplitude (Q_T = 1.365(13) Å) is only slightly greater than for 1. The benzimidazoles are syn-disposed in quasi-axial positions, with an angle of 105.5(3)° between their mean planes. The presence of the benzimidazoles requires two of the torsion angles to be close to zero, and consequently flattens the boat moiety of the cycle.

The coordinated EtO^- anions are disordered about a two-fold axis passing through the O-atom and a point on the C-C bond, and were refined with equal population parameters. The observation of EtO^- anions was surprising since the only base present in solution during the synthesis was the free ligand, and ethanol is more difficult to deprotonate than H_2O (present
from the H₂O of crystallization of the Cu²⁺ perchlorate. Furthermore, benzimidazoles coordinated to Cu²⁺-atom are deprotonated even by weak bases [10], and a deprotonation of the ligand might have been expected rather than the formation of a hydroxo complex. It is, therefore, necessary to seek some effect which will stabilize the ethoxy bridge, and examination of a space-filling representation of the structure of 2 suggests that the benzimidazoles and the aliphatic bridging chain form a hydrophobic pocket around the Cu₂O₃ core, and thus the coordination of an EtO group might be more favorable than a OH group.

The non-coordinated EtOH molecule is also disordered, and was refined as two separate molecules each with a population parameter of 50%. They form H-bonds to a N–H group of a benzimidazole (N–O distances 2.76(3) and 2.73(3)Å). The ClO₄⁻ anion is not disordered, but forms a H-bond with the benzimidazole N–H group which is not bound to the EtOH (O–N distance 2.91(2)Å).

Conclusion

The flexibility of L³ and L⁴ allows them to act as bidentate ligands rather than as bis-monodentate ligands as observed for L¹ and L². Although, by tradition, coordination chemists have tended to study ligands forming five- or six-membered chelate rings, the two structures presented here show that larger rings may readily be formed. The very flexibility of the chelate ring allows the bite angle to vary by 30° while maintaining the same Cu–N bond distance. When the bite angle of the chelate ring is reduced, the metal ion packers up out of the mean plane of the chelate ring, which then forms a hydrophobic region around the metal ion, whereas, if the metal ion lies in the plane of the chelate ring, the non-polar regions of the ligand lie away from the metal. This possibility of using a large chelate ring to generate a hydrophobic region around a metal ion is currently being investigated in our laboratories.

Experimental

Synthesis of 1,3-Bis(1-methylbenzimidazol-2-yl)propane (L¹)

A mixture of 6.6 g (0.05 mol) of 1,3-propanedicarboxylic acid, 11.9 g (0.11 mol) benzene-1,2-diamine and 100 ml H₃PO₄ (85%) were heated at 180° with mechanical stirring for 3 h. After cooling, the dark blue soln. was poured into 2 l of H₂O, and the resulting precipitate filtered and suspended in 500 ml of aq. NH₄Cl (12%). The precipitate was treated with activated carbon in MeOH, and recrystallized from MeOH/H₂O to give 12.8 g of ligand L¹ (82%). ¹H-NMR (400 MHz, D₂O (DMSO)) 12.1 (br. s, 2 H); 7.46 (m, 4 H); 7.10 (m, 4 H); 2.91 (t, 4 J=7.5, 4 H); 2.29 (q, 3 J=5.7, 2 H). MS: 277 (23, [M+H⁺]), 145 (100), 132 (96), 92 (23).

Synthesis of 1,3-Bis(1-methylbenzimidazol-2-yl)propane (L²)

L² was methylated as described in [5], and recrystallized from MeCN. M. p. 172–175°. ¹H-NMR (200 MHz, CDC1₃) 7.68 (m, 4 H); 7.23 (m, 4 H); 3.72 (s, 6 H); 3.08 (s, 4 H); 2.50 (q, 2 H). MS: 305 (8, [M+H⁺]), 159 (100), 146 (80), 131 (51), 104 (19).

Synthesis of 1,3-Bis(1-methylbenzimidazol-2-yl)propane(acetonitrile)copper(I) Hexafluorophosphate. [Cu(L¹)(MeCN)]PF₆ (L⁴)

(Cu(MeCN)₄(PF₆)₂(12)0.246 g (0.66 mmol) was dissolved in 15 ml of degassed MeCN under N₂, 0.200 g (0.66 mmol) of L² dissolved in 10 ml CH₂Cl₂ under N₂, and the CH₂Cl₂ evaporated under vacuum to avoid precipitation of the unreacted Cu salt. Diffusion of eth as the soln. under N₂ gave colorless crystals of quality suitable for X-ray diffraction. Analysis: found: C 46.6, H 4.4, N 12.75; calc.: C 45.5, H 4.5%, N 12.6.

X-Ray Crystal Structure Determinations

[Cu(C₂H₄N₂)₂(MeCN)PF₆] PF₆, M = 554.0, triclinic, P1, a = 7.537(1), b = 12.357(1), c = 14.286(2) Å, α = 65.18(1)°, β = 75.75(1)°, γ = 82.33(1)°, V = 1169.7(3) Å³, Z = 2, Dₓ = 1.57 g·cm⁻³. Mo(Kα), λ = 0.71069 Å, μ = 1.057 mm⁻¹, F(000) = 564. 3254 unique reflections measured at r.t., 2427 observed (IφL ≥ 4σ(I)), R = 0.058 using unit weights for 310 variables with all non-hydrogen atoms refined with anisotropic displacement parameters. [Cu(C₂H₄N₂)₂(MeCN)₂(2)ClO₄⁻(EtOH)₂, M = 1062.9, monoclinic, P2₁, a = 9.848(2) Å, b = 13.000(2), c = 18.759(3) Å, β = 96.46(1)°, V = 2385.27(7) Å³, Z = 2, Dₓ = 1.48 g·cm⁻³. Mo(Kα), λ = 0.71069 Å, μ = 1.072 mm⁻¹, F(000) = 1104. 3749 unique reflections measured, 3717 observed (IφL ≥ 4σ(I)), R = 0.074 using unit weights for 293 variables with all non-H-atoms except the disordered EtOH groups refined with anisotropic displacement parameters. Structures were solved by direct methods [12], and all other calculations used the XTAL [13] and ORTEP II [14] programs. Full details of the crystal-structure determination will be published elsewhere [15].

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