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SYNTHESIS, PROPERTIES AND MOLECULAR STRUCTURES OF COBALT(II), COPPER(II) AND ZINC(II) COMPLEXES WITH 1,2-BIS[3-(PYRAZOL-1-YL)-2-OXAPROPYL]BENZENE

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Abstract—The new ligand 1,2-bis[3-(pyrazol-1-yl)-2-oxapropyl]benzene (L), reacted with cobalt(II) chloride, copper(II) chloride and zinc(II) chloride to form $[CoLCl_2]$, $[CuLCl_2]$ and $[ZnLCl_2]$, respectively. The structures of these metal complexes have been determined by X-ray crystallography. The Co and Zn structures are isomorphous with distorted tetrahedral metal geometries. The coordination sphere of the copper(II) ion in its complex is intermediate between distorted tetrahedral and distorted square-pyramidal geometry, if a weak Cu···O interaction is taken into account.

Polyfunctional ligands derived from pyrazole,[1–4] imidazole[5–8] and pyridazine[9–11] form transition-metal complexes in which metals are brought into proximity because of the N-donor sites that coordinate to metals in the systems. Structural characterizations of these molecules are vigorously pursued in many laboratories because these compounds served as potential models for biological dimetallic sites.[12–14] Some dicopper(II) complexes with pyrazolyl ligands are potential models for haemocyanin.[15]

In an effort to develop new polynuclear complexes, we were interested in metal complexation of polyfunctional pyrazole ligands. The previously prepared 4-methyl-2,6-bis(pyrazolyl-1-ylmethyl)phenol ligand reacted with Zn^{II} to give a binuclear complex.[16] 1,3,5-Tri(pyrazolyl-1-yl methyl)benzene[17] reacted with Cu^{II} to give polymeric bis(μ-chloro)copper(II) complexes. Other novel ligands, 1,2-bis(pyrazolyl-1-ylmethyl)benzene[18] and 5-methyl-1,3-bis(pyrazolyl-1-ylmethyl)benzene,[19] were prepared and their abilities to complex with Cu^{II} and Co^{II} ions were reported. Here we report an investigation of the complexing properties of the new pyrazolyl ligand, 1,2-bis[3-(pyrazol-1-yl)-2-oxapropyl]benzene, which is a bidentate ligand with two N-donor sites in the pyrazoyl rings. The crystal structures of its cobalt(II), copper(II) and zinc(II) complexes and spectral properties are described.

EXPERIMENTAL

Chemicals

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. N-hydroxymethylpyrazole[20] and 1,2-bis(bromomethyl)benzene[21] were prepared according to the literature method.

Physical methods

Melting points were obtained with a Thomas–Hoover capillary apparatus in open capillaries and are uncorrected. Proton NMR spectra were recorded on a Bruker AM-300WB instrument at 300 MHz using $CDCl_3$ and DMSO as solvents. EPR spectra were recorded on a Bruker ESP 300 X-band instrument using diphenylpicryhydrazyl (dpph) as standard. Magnetic susceptibilities were measured

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using the Faraday method on a CAHN 200 instrument with $Hg[Co(SCN)_4]$ as standard; diamagnetic corrections were made using Pascal's parameters. IR spectra were recorded on a Perkin–Elmer 983G analyser and elemental analyses were obtained using a Perkin–Elmer 2400 analyser. UV spectra were recorded on a Hitachi U-3210 spectrophotometer.

Syntheses

1,2-*Bis*[3-(*pyrazol*-1-*yl*)-2-*oxapropyl*]*benzene* (*L*). Sodium hydride oil dispersion (0.50 g) was added to a solution of N-hydroxymethylpyrazole (1.96 g, 20 mmol) in dry THF (50 cm^3) under nitrogen. The solution was heated to reflux for 12 h and then cooled to room temperature. A solution of 1,2-bis(bromomethyl)benzene (2.64 g, 10 mmol) in dry THF (25 cm^3) was added dropwise with stirring. The resulting mixture was stirred at room temperature for 2 h and then refluxed overnight. After cooling to room temperature, water was added dropwise to destroy excess NaH and the solution was evaporated to dryness. The residue was taken up in water (40 cm^3) and extracted with $CHCl_3$ (3×50 cm^3). The chloroform extracts were dried with anhydrous $MgSO_4$ and evaporated to give the crude product as a yellow oil. The product was purified by chromatography (silical gel 60) using ethyl acetate–hexane (1:4) ($R_f = 0.4$) as eluent to give a pale yellow oil (yield, 1.4 g, 47%). ^1H NMR ($CDCl_3$): δ 4.46 (4H, s, aryl CH_2O), 5.38 (4H, s, methylene bridges), 6.30 (2H, t, $J = 2$Hz, pyrazolyl ^4CH), 7.20–7.29 (4H, m, aryl H), 7.52 (2H, d, $J = 2$Hz, pyrazolyl ^5CH), and 7.54 (2H, d, $J = 2$Hz, pyrazolyl ^3CH).

[*CoLCl*$_2$]. Cobalt(II) chloride hexahydrate (238 mg, 1 mmol) in methanol (15 cm^3) was added to a methanolic solution (10 cm^3) of L (267 mg, 1 mmol). The mixture was stirred for 10 min at room temperature and filtered. The blue crystalline product was obtained by slow diffusion of diethyl ether into the mixture, m.p. 196–197°C. Found: C, 45.3; H, 3.9; N, 13.3 Calc. for $C_{16}H_{18}Cl_2CoN_4O_2$: C, 45.0; H, 4.2; N, 13.1%. IR: ν_{max} (cm^{-1}) 3114m, 1520m, 1439m, 1409m, 1278m, 1089s, 1047m, 748m. λ_{max}/nm (DMF) 672 (ε 340 $dm^3\,mol^{-1}\,cm^{-1}$), 608 (ε 210 $dm^3\,mol^{-1}\,cm^{-1}$), 233 (ε 1486 $dm^3\,mol^{-1}\,cm^{-1}$).

[*CuLCl*$_2$]. Copper(II) chloride dihydrate (170 mg, 1 mmol) and L (267 mg, 1 mmol) were dissolved in methanol (15 cm^3). The mixture was allowed to stand at room temperature. Yellowish-green crystals formed which were filtered, washed with methanol then with diethyl ether and air-dried, yield 0.29 g (67%); m.p. 166–167°C (dec.). Found: C, 44.6; H, 3.9; N, 12.6 Calc. for $C_{16}H_{18}Cl_2CuN_4O_2$: C, 44.4; H, 4.2; N, 12.9%). IR: ν_{max} (cm^{-1}) 3110m, 1510m, 1404m, 1387m, 1204m, 1103s, 1057s, 990m, 756m. λ_{max}/nm (DMF) 436 (ε 250 $dm^3\,mol^{-1}\,cm^{-1}$), 271 (ε 3676 $dm^3\,mol^{-1}\,cm^{-1}$), 233 (ε 2077 $dm^3\,mol^{-1}\,cm^{-1}$).

[*ZnLCl*$_2$]. The same procedure as described for [$CuLCl_2$] was followed using $ZnCl_2$, resulting in the isolation of colourless crystals, yield 0.29 g (58%); m.p. 188–189°C Found: C, 44.2; H, 4.3; N, 12.6. Calc. for $C_{16}H_{18}Cl_2N_4O_2Zn$: C, 44.2; H, 4.1; N, 12.9%). IR: ν_{max} (cm^{-1}) 3115m, 1523m, 1410m, 1280m, 1091s, 1052s, 915m, 768m, 748m. ^1H NMR (DMSO): δ 4.46(2H,s), 5.45(4H,s), 6.35(2H,t), 7.27(4H,m), 7.56(2H,d), 7.89(2H,d). λ_{max}/nm (DMF) 226 (ε 918 $dm^3\,mol^{-1}\,cm^{-1}$).

Structure determination

Suitable crystals of [$CoLCl_2$], [$CuLCl_2$] and [$ZnLCl_2$] complexes were chosen. Intensity data were collected at room temperature on a CAD-4 diffractometer using monochromated Mo-K_α radiation (λ 0.71073Å) for Co and Zn and Cu-K_α radiation (λ 1.5406Å) for Cu complexes. The unit-cell parameters were derived from a least-squares refinement of 25 setting reflections for [$CuLCl_2$] and 24 setting reflections for [$CoLCl_2$] and [$ZnLCl_2$]. The θ–2θ scan technique and a variable scan speed was used to obtain the integrated intensities. Three reference reflections were monitored throughout the measurement; the absorption intensities were less than 3% in three cases. Absorption corrections were applied according to an experimental ψ rotation curve. Other details of the crystal data appear in Table 1.

The structures were solved by the heavy-atom method; subsequent Fourier syntheses based on the heavy atom revealed the positions of all non-hydrogen atoms. Least-squares refinement including anisotropic thermal parameters for all non-hydrogen atoms was performed. For [$CoLCl_2$] and [$ZnLCl_2$] crystals a unit weighting of the form $1/\sigma^2(F_o)$ was used and for [$CoLCl_2$] crystals a unit weight was used. All hydrogen-atom parameters were calculated according to ideal geometry and were not refined. The structural analyses were carried out on a Microvax III computer using NRCVAX programs.[22] Atomic scattering factors were taken from ref. 23.

Additional material sent to the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1. Crystallographic data for $[CoLCl_2]$, $[CuLCl_2]$ and $[ZnLCl_2]$ complexes

Complex	$[CoLCl_2]$	$[CuLCl_2]$	$[ZnLCl_2]$
Formula	$C_{16}H_{18}Cl_2CoN_4O_2$	$C_{16}H_{18}CuCl_2N_4O_2$	$C_{16}H_{18}Cl_2N_4O_2Zn$
Formula weight	428.18	432.80	434.63
Crystal size (mm)	$0.20\times0.25\times0.30$	$0.20\times0.30\times0.35$	$0.25\times0.30\times0.35$
Crystal	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pbca$	$P2_1/n$
Z	4	8	4
a (Å)	7.717(4)	13.988(6)	7.689(2)
b (Å)	16.816(6)	14.713(2)	16.788(3)
c (Å)	14.676(5)	17.431(7)	14.739(4)
α (°)			
β (°)	99.43(3)		98.91(2)
γ (°)			
V (Å^3)	1878.9(12)	3587.6(21)	1878.5(8)
$F(000)$	876	1768	888
D_c (Mg m^{-3})	1.514	1.603	1.537
μ (mm^{-1})	1.21	4.66	3.60
$2\theta_{max}$ (°)	45.0	110.0	45.0
Ranges of h, k, l	−8–8, 0–18, 0–15	0–14, 0–15, 0–18	−8–8, 0–18, 0–15
Scan parameter	$2(0.90+0.35\tan\theta)$	$2(1.00+0.15\tan\theta)$	$2(0.75+0.35\tan\theta)$
Total number of reflections	2249($1328>2\sigma$)	2258($2107>2\sigma$)	2452($1899>2\sigma$)
R^a	0.044	0.047	0.030
Rw^b	0.030	0.051	0.022
GoF^c	1.32	3.34	1.97

$^a R=\Sigma\|F_o-F_c\|/\Sigma\|F_o\|$

$^b Rw=[\Sigma w(F_o-F_c)^2/\Sigma wF_o^2]^{1/2}$.

^{c} GoF $=[\Sigma w(F_o-F_c)^2/$(No. of reflns.-No. of params.)$]^{1/2}$.

RESULTS AND DISCUSSION

Synthesis

The ligand, 1,2-bis[3-(pyrazol-1-yl)-2-oxapropyl]benzene (L), which possesses two nitrogen donor sites in the pyrazolyl rings, was prepared. Reactions of metal ions and the ligand result in the formation of complexes $[CoLCl_2]$, $[CuLCl_2]$ and $[ZnLCl_2]$, which are mononuclear complexes.

Description of the structure

The crystal structures of $[CoLCl_2]$, $[CuLCl_2]$ and $[ZnLCl_2]$ complexes are depicted in Fig. 1 and Fig. 2, and selected bond distances and angles are listed in Table 2. The structure of the $[ZnLCl_2]$ complex is similar to that of the $[CoLCl_2]$ complex, the two crystals being isomorphous. In $[CoLCl_2]$ the coordination of the cobalt(II) ion is a slightly distorted tetrahedral geometry. The Co^{II} ion is surrounded by two nitrogen atoms [N(1), N(3)] from the pyrazolyl ring of the ligand and two chlorines [Cl(1), Cl(2)]. Two Co—N distances, 2.010(5) and 1.991(5) Å for $[CoLCl_2]$ are common for M—N distances. Two Co—Cl distances are 2.240(2) Å in the $[CoLCl_2]$ complex. In the $[CoLCl_2]$ complex the Co—O distances, 3.423(4) and 3.386(5) Å, are too long to be considered as bonding. The angle N(1)—Co—N(3) is 115.74(21), Cl(1)—Co—Cl(2) is 114.37(9) and Cl(1)—Co—N(1) is 107.47(16)°, showing slight distortion away from the ideal tetrahedral geometry.

In $[CuLCl_2]$, the copper (II) ion is coordinated by

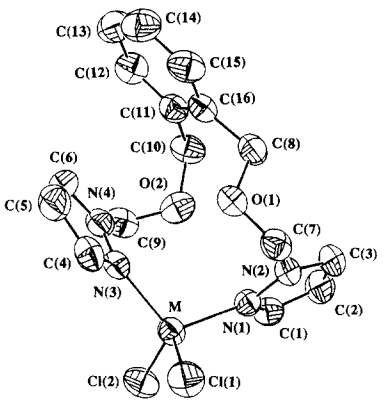

Fig. 1.

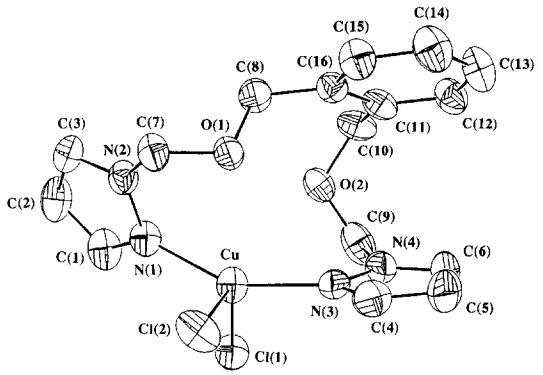

Fig. 2.

two pyrazolyl nitrogen atoms at Cu—N(1) 1.969(5) and Cu—N(3) 1.984(5) Å, and two chlorines at Cu—Cl(1) 2.269(2) and Cu—Cl(2) 2.289(2) Å. The coordination sphere of copper(II) can be described as a distorted tetrahedral geometry with angles ranging from 94.29(14) to 152.45(19)°. However, the angle of N(1)—Cu—N(3), 152.45(19)°, deviates much from the ideal tetrahedral angles. The Cu—O(1) distance, 2.738(4) Å, is close to that of [Cu(1,6-bis(benzimidazol-2-yl)-2,5-dioxahexane)Br_2][24] [2.743(6) Å] and is shorter than that of Cu—O(2), 3.233(4) Å and those of Co—O. It cannot be excluded that some bonding also occurs from Cu to the oxygen atom O(1). The geometry of the copper(II) ion environment can thus be described as intermediate between distorted tetrahedral and square-pyramidal geometry.

Comparison of the structures of [$CoLCl_2$], [$CuLCl_2$] and [$ZnLCl_2$] indicates that 1,2-bis[3-(pyrazol-1-yl)-2-oxapropyl]benzene is a flexible ligand. Due to this flexibility its mode of coordination strongly depends on the preference of the metal ions for specific coordination geometry. In [$CoLCl_2$] and [$ZnLCl_2$] the metal ion has a common tetrahedral coordination and the ligand acts as a bidentate ligand. The copper ion has a square-pyramidal coordination in [$CuLCl_2$] and the ligand acts as a tridentate ligand. For these complexes the distances of metal–nitrogen are within the ranges observed for other complexes.[15–19] In these complexes, the pyrazole rings are planar and the methyl carbons are coplanar with the respective pyrazole ring.

Spectroscopy

In the IR spectra the C—H stretching vibrations of the pyrazolyl groups in three complexes are at

Table 2. Selected bond distances (Å) and angles (°) for [$CoLCl_2$], [$CuLCl_2$] and [$ZnLCl_2$] complexes; for the atom numbering see Figs 1 and 2

[$CoLCl_2$]			
Co—Cl(1)	2.240(2)	Co—Cl(2)	2.240(2)
Cc—N(1)	2.010(5)	Co—N(3)	1.991(5)
Co—O(1)	3.423(4)	Co—O(2)	3.386(5)
Cl(1)—Co—Cl(2)	114.37(9)	Cl(1)—Co—N(1)	107.47(16)
Cl(1)—Co—N(3)	104.51(16)	Cl(2)—Co—N(1)	103.00(16)
Cl(2)—Co—N(3)	112.02(16)	N(1)—Co—N(3)	115.74(21)
[$CuLCl_2$]			
Cu—Cl(1)	2.269(2)	Cu—Cl(2)	2.289(2)
Cu—N(1)	1.969(5)	Cu—N(3)	1.984(5)
Cu—O(1)	2.738(4)	Cu—O(2)	3.233(4)
Cl(1)—Cu—Cl(2)	120.02(7)	Cl(1)—Cu—O(1)	153.88(9)
Cl(1)—Cu—N(1)	94.29(14)	Cl(1)—Cu—N(3)	98.48(14)
Cl(2)—Cu—N(1)	97.82(14)	Cl(2)—Cu—O(1)	84.53(9)
Cl(2)—Cu—N(3)	96.74(15)	O(1)—Cu—N(1)	72.02(15)
O(1)—Cu—N(3)	86.27(15)	N(1)—Cu—N(3)	152.45(19)
[$ZnLCl_2$]			
Zn—Cl(1)	2.224(1)	Zn—Cl(2)	2.226(1)
Zn—N(1)	2.029(3)	Zn—N(3)	2.014(3)
Zn—O(1)	3.495(3)	Zn—O(2)	3.476(3)
Cl(1)—Zn—Cl(2)	116.32(5)	Cl(1)—Zn—N(1)	109.11(8)
Cl(1)—Zn—N(3)	104.70(9)	Cl(2)—Zn—N(1)	103.39(9)
Cl(2)—Zn—N(3)	112.77(8)	N(1)—Zn—N(3)	111.64(11)

3114, 3110 and 3115 cm^{-1}, and the C=N stretching vibrations at 1520, 1510 and 1523 cm^{-1}. The ^1H NMR signals of the $[ZnLCl_2]$ complex showed a small positive chemical shift relative to those of the ligand. However, there is a large positive chemical shift of pyrazolyl C^3H at δ7.89 ppm relative to that of the ligand at δ 7.54 ppm (see Experimental section).

The X-band EPR spectra of these polycrystalline complexes were measured at room temperature. The EPR spectrum of $[CuLCl_2]$ is similar to those of $[Cu(bmdhp)(H_2O)(ClO_4)]_2$[25] [bmdhp = 1,7-bis(N-methyl-benzimidazol-2-yl)-2,6-dithiaheptane] and $[Cu(1,3,5\text{-tri(pyrazolyl-1-ylmethyl)benzene})_2(ClO_4)_2(H_2O)_2]$,[17] and shows an axial signal.[26] The g value ($g_\parallel = 2.225$, $g_\perp = 2.158$) of the $[CuLCl_2]$ complex is consistent with a square-pyramidal coordination sphere for copper(II) and the single unpaired electron is located in an essentially $d_{x^2-y^2}$ orbital. The EPR spectra of the $[CoLCl_2]$ complex at room temperature show no signal, but a broad isotropic signal at 77 K with the g value 3.589. The magnetic moment was measured at room temperature. The magnetic moments (μ_{eff}) of $[CoLCl_2]$ and $[CuLCl_2]$ complexes are 4.58 and 1.92 B.M., respectively. The value for $[CoLCl_2]$ indicates that the tetrahedral cobalt(II) ion (d^7-configuration) has high spin ($S = 3/2$)[27] in $[CoLCl_2]$.

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