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SYNTHESIS AND CRYSTAL STRUCTURE OF A NOVEL DINUCLEAR COMPLEX OF COBALT(II) WITH A NEW BENZIMIDAZOLE-CONTAINING AZACYCLE LIGAND

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Abstract—A novel dicobalt(II) complex $Co_2Cl_4L_2 \cdot C_2H_5OH$ was obtained, where L is [4′-(2″-methylene-benzimidazole-yl)-1′,4′-dinitrogencyclohexane]^{1,2}-benzimidazole, a new azacycle ligand. The single crystal structure of the complex was determined by X-ray diffraction. Two nitrogen and two chloride atoms are around each cobalt with tetrahedral geometry. Each L bonds two cobalt atoms through its two benzimidazole groups.

Benzimidazole transition metal complexes are of great interest because of relevance to metalloproteins such as haemoglobin, haemocyanins and blue-copper proteins.[1,2] They also are used as mimics of the self-assembling processes.[3] Reed *et al.* found that copper can promote auto-oxidation of the benzimidazole containing polydentate ligand 2-hydroxyl - N,N,N′,N′ - tetra(N‴′- ethylbenzimidazolyl-methyl)-1,3-diamine.[4] When preparing the cobalt(II) complex of N,N,N′,N″,N″-pentabenzimidazolylmethyl diethylene triamine, we also obtained a new dicobalt complex with a new azacycle ligand, [4′-(2″-methylene-benzimidazole-yl)-1′,4′ - dinitrogencyclohexane]^{1,2} - benzimidazole, which may come from the oxidation of pentabenzimidazolylmethyl diethylenetriamine. In this paper we report the structure of the dicobalt(II) complex with the new azacycle ligand.

EXPERIMENTAL

Synthesis and preparation of $Co_2Cl_4L_2 \cdot C_2H_5OH$

$CoCl_2 \cdot 6H_2O$ 2 mmol ethanol solution was added to an ethanol solution containing 1 mmol N,N,N′,N″,N″-pentabenzimidazolylmethyl diethylene triamine (L1)[5] with stirring at 60–70°C and sky blue microcrystals were deposited. The solution mixture was heated to reflux for about 2 h, then cooled. The solid substance was collected and washed with ethanol, then dried at room temperature. The product was added to about 50 cm^3 ethanol. The solid–liquid mixture was heated for several hours. Only a little solid dissolved and a light blue–grey solution was obtained. The solid and the solution were separated by filtration. The solid was dried *in vacuo* over P_2O_5. Found: C, 45.1; H, 3.8; N, 15.8; Co, 14.5. Calc. for $Co_3Cl_6[L1] \cdot 2H_2O$: C, 44.8; H, 4.0; N, 15.4; Co, 14.9%.

The light blue–grey solution was kept at room temperature and evaporated very slowly for about 6 months. The title single crystals ($Co_2Cl_4L_2 \cdot C_2H_5OH$) used for X-ray diffraction were obtained.

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X-Ray data collection, structure determination and refinement for complex $Co_2Cl_4L_2 \cdot C_2H_5OH$

A transparent blue crystal of $C_{38}H_{40}Cl_4Co_2N_{10}O$, having approximate dimensions $0.15 \times 0.2 \times 0.2$ mm was mounted on a glass fibre in a random orientation. The determination of the unit cell and the data collection were performed with Mo-K_α radiation ($\lambda = 0.71073$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite crystal monochromator. A total of 3130 independent reflections were collected in the range of $2° \leqslant \theta \leqslant 23°$ by the ω–2θ scan technique at room temperature (23 ± 1°C) in which 1426 reflections with $[I \geqslant 3\sigma(I)]$ were considered to be observed and used in the succeeding refinement. A correction for Lp effects was applied to the data.

Crystals are othorhombic, space group $P2_12_12_1$, with $a = 10.331(3)$, $b = 14.808(4)$, $c = 25.862(5)$ Å, $V = 3956.4(3)$ Å^3, $M_r = 912.49$, $Z = 4$, $D_x = 1.53$ g cm^{-3}, $\mu = 11.54$ cm^{-1}, $F(000) = 1872$.

The structure was solved by Direct Methods (MULTAN 82). The positions of the two cobalt atoms and one chloride atom were located on an E-map. All the other non-hydrogen atoms were determined from successive difference Fourier syntheses.

The final refinement by full-matrix least-squares with anisotropic thermal parameters for non-hydrogen atoms converged with agreement factors of $R = \Sigma|\Delta F|/\Sigma|F_0| = 0.061$ and $Rw = [\Sigma w|\Delta F|^2/\Sigma|F_0|^2]^{1/2} = 0.068$ (unit weights for all observed reflections). The highest peak on the final difference Fourier map had a height of 0.55 eÅ^{-3}.

All calculations were performed on a PDP 11/44 computer using the SDP/PLUS program system.

RESULTS AND DISCUSSION

Figure 1 shows the molecular structure of the complex $Co_2Cl_4L_2 \cdot C_2H_5OH$. The final atomic positional and thermal parameters, and some bond lengths and bond angles are given in Table 1. Tables of final atomic positional and thermal parameters, full lists of bond lengths and angles, and equations of least-squares plane have been deposited as supplementary material with the Editor.

The structure of the title ligand L is determined from the dicobalt complex structure which shows that L is a bidentate ligand. Two benzimidazole nitrogen atoms are the coordinating atoms. Each cobalt(II) ion is bonded to two benzimidazole nitrogen atoms which come from two different azacycle ligands. L acts as a bridging ligand. The mean Co—N distance is 2.014 Å for Co(1) and 2.037

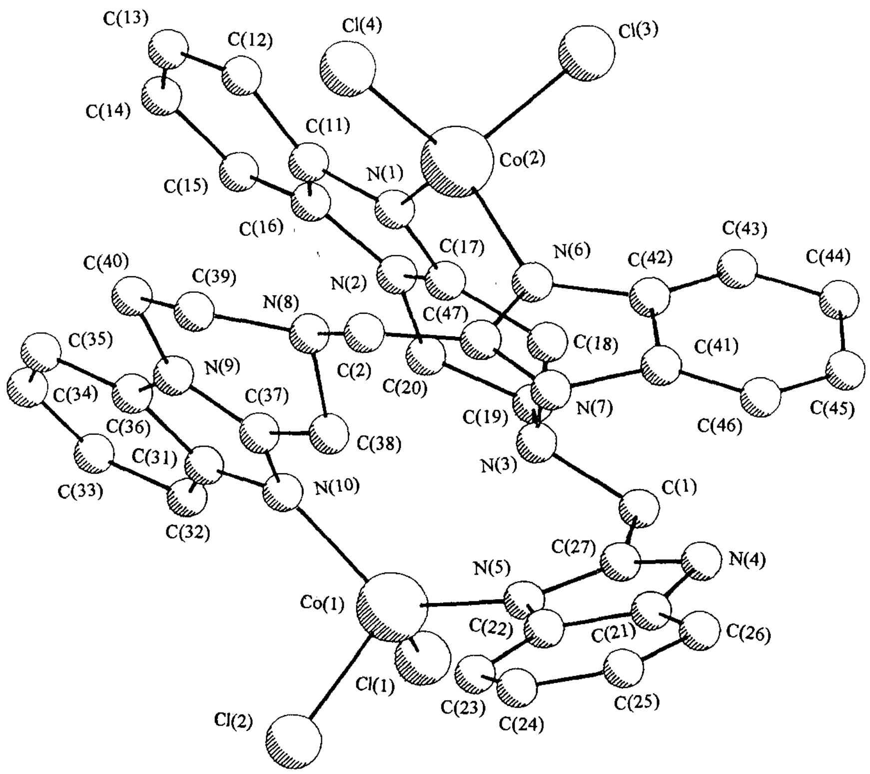

Fig. 1. Perspective view of the $Co_2Cl_4L_2 \cdot C_2H_5OH$.

Table 1. Selected bond distances (Å) and angles (°)

Co(1)—Cl(1)	2.261(3)	Co(1)—N(5)	2.013(7)
Co(1)—Cl(2)	2.285(3)	Co(1)—N(10)	2.014(8)
Co(2)—Cl(3)	2.238(4)	Co(2)—N(1)	1.999(8)
Co(2)—Cl(4)	2.270(3)	Co(2)—N(6)	2.074(9)
N(1)—C(11)	1.46(1)	N(6)—C(42)	1.42(1)
N(1)—C(17)	1.34(1)	N(6)—C(47)	1.35(1)
N(2)—C(16)	1.38(1)	N(7)—C(41)	1.43(1)
N(2)—C(17)	1.37(1)	N(7)—C(47)	1.33(1)
N(2)—C(20)	1.50(1)	N(8)—C(2)	1.47(1)
N(3)—C(1)	1.49(1)	N(8)—C(38)	1.49(1)
N(3)—C(18)	1.50(1)	N(8)—C(39)	1.49(1)
N(3)—C(19)	1.47(1)	N(9)—C(36)	1.38(1)
N(4)—C(21)	1.41(1)	N(9)—C(37)	1.30(1)
N(4)—C(27)	1.35(1)	N(9)—C(40)	1.53(1)
N(5)—C(22)	1.39(1)	N(10)—C(31)	1.38(1)
N(5)—C(27)	1.34(1)	N(10)—C(37)	1.34(1)
C(1)—C(27)	1.51(1)	C(2)—C(47)	1.50(1)
C(19)—C(20)	1.50(1)	C(39)—C(40)	1.52(2)
Cl(1)—Co(1)—Cl(2)	103.5(1)	Cl(2)—Co(1)—N(5)	105.0(3)
Cl(1)—Co(1)—N(5)	115.9(2)	Cl(2)—Co(1)—N(10)	97.3(2)
Cl(1)—Co(1)—N(10)	115.7(2)	N(5)—Co(1)—N(10)	116.0(3)
Cl(3)—Co(2)—Cl(4)	109.2(1)	Cl(4)—Co(2)—N(1)	118.4(3)
Cl(3)—Co(2)—N(1)	98.2(3)	Cl(4)—Co(2)—N(6)	108.3(3)
Cl(3)—Co(2)—N(6)	107.6(3)	N(1)—Co(2)—N(6)	114.2(3)
Co(2)—N(1)—C(11)	127.2(6)	Co(2)—N(6)—C(42)	127.3(7)
Co(2)—N(1)—C(17)	125.8(7)	Co(2)—N(6)—C(47)	123.5(7)
C(11)—N(1)—C(17)	105.1(8)	C(42)—N(6)—C(47)	107.5(8)
C(16)—N(2)—C(17)	109.4(9)	C(41)—N(7)—C(47)	106.0(8)
C(16)—N(2)—C(20)	128.4(8)	C(2)—N(8)—C(38)	110.0(7)
C(1)—N(3)—C(18)	109.1(7)	N(6)—C(47)—N(7)	113.2(9)
C(1)—N(3)—C(19)	110.5(8)	N(6)—C(47)—C(2)	112(1)
C(18)—N(3)—C(19)	106.8(7)	N(7)—C(47)—C(2)	124.2(9)
N(1)—C(17)—N(2)	111(1)	N(1)—C(17)—C(18)	126.1(9)
N(2)—C(17)—C(18)	123.0(9)	N(3)—C(18)—C(17)	107.1(8)
N(3)—C(19)—C(20)	111.4(8)	N(2)—C(20)—C(19)	109.1(8)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2. Dihedral angles between planes

Plane no.	Plane no.	Dihedral angle (°)
1	2	8.31
1	3	112.83
1	4	6.29
1	6	115.73
3	4	116.69
3	6	25.72
4	5	3.47
4	6	116.76

Å for Co(2). The distances of Co(1)—N(5) and Co(1)—N(10) are almost the same for cobalt(1). For cobalt(2) the Co(2)—N(6) is longer than Co(2)—N(1). The other two coordinating atoms for each cobalt(II) are two chloride atoms. The mean distance for Co—Cl is 2.273 and 2.254 Å respectively for Co(1) and Co(2). The four atoms around each cobalt are in a tetrahedral configuration.

The C(11)–C(17), N(1), N(2) and Co(2) atoms lie approximately in a plane (plane 1). The maximum deviation from plane 1 is −0.37 Å [Co(2)]. The distance between Co(2) and plane 6 which consists of C(41)—C(47), N(6) and N(7) is 0.51 Å. The Co(1) atom simultaneously lies in plane 3 [C(21)–C(27), N(4), N(5)] and plane 4 [C(31)–C(37), N(9), N(10)]. The maximum deviations from the planes are −0.28 and 0.29 Å for plane 3 and plane 4, respectively [Co(1)]. C(17)–C(20) atoms make up plane 2 and C(37)–C(40) plane 5. The maximum deviation from plane 2 is 0.759 Å [N(3)], and plane 5 −0.675 Å [N(8)]. Some dihedral angles between planes are given in Table 2.

The two cobalt atoms differ little in the molecular structure of the title complex.

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