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Preparation, Properties and Molecular Structure of a Binuclear Pyridine-2,6-dicarboxylate-*N*-oxide Copper(II) Complex

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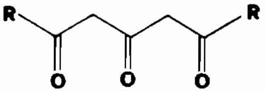
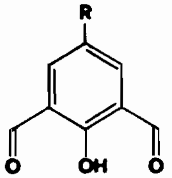
β,δ-Triketones, diformyl-phenols, keto-thiophenols and keto-carboxylic acids (I–V) have been extensively used to prepare homo- and hetero-dinuclear complexes [1–4]. In these complexes two metal ions share the central donor atom and interact through oxygen bridging. Many complexes with pyridine-*N*-oxides, which are well known as bridging agents, have been characterized and studied and a particular interest has been devoted to the magnetic interaction between the metal ions [5].



I



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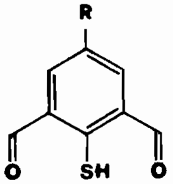

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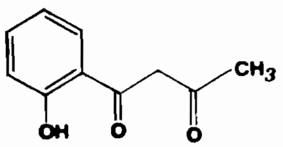

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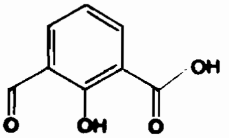
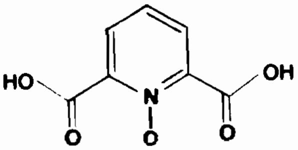


V

Pyridine-2,6-dicarboxylic acid-*N*-oxide (H_2-PDCNO) (VI) can be considered (to act) as a binucleating ligand, although it is well known that polycarboxylic acids often form polymeric complexes through their carboxylate groups [6, 7].



(H_2PDCNO)

VI

In order to have a more appropriate knowledge of the coordination behaviour of this ligand, we examined the reaction of copper(II) with the pyridine-2,6-dicarboxylic acid-*N*-oxide.

Experimental

Pyridine-2,6-dicarboxylic acid-*N*-oxide, solvents and products were reagent grade used without further purification.

Synthesis

[Cu(PDCNO)(py)(MeOH)]$_2$ was prepared by reaction of pyridine-2,6-dicarboxylic acid-*N*-oxide (1 mmol) with LiOH (2 mmol) and $Cu(CH_3COO)_2 \cdot 4H_2O$ (1 mmol) in methnaol and in the presence of a few drops of pyridine. The resulting solution, clarified and left standing for a week, separates good blue crystals. *Anal.* Calc. for $(C_{14}H_{14}N_2O_5Cu)_2$ C, 43.88; H, 3.40; N, 7.87. Found: C, 43.56; H, 3.25; N, 7.46%.

X-ray Data

Well formed crystals of [Cu(PDCNO)(py)(MeOH)]$_2$ suitable for X-ray work, were mounted on a glass fibre and covered with epoxy adhesive to prevent crystal air decomposition. Cell constants were determined from a least-squares refinement of the setting angles of 25 reflexions, which had been carefully centered on a Philips PW1100 diffractometer. The observed intensities were corrected for Lorentz polarization (Lp) and for absorption [8]. Crystal and intensity data are reported in Table I. The structure was solved by standard methods and refined to the final conventional R of 7.2%, when the maximum shift on the refined parameters was 0.2σ and the maximum residual of electronic density was 1 e/Å^3. Scattering factors for neutral atoms were taken from ref. 9. Positional and thermal parameters are listed in Table II, bond distances and angles in Table III. Calculations were performed using the SHELX program system [10].

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TABLE I. Crystals and Intensity Data for $[Cu(PDCNO)(py)(MeOH)]_2$

$C_{26}H_{24}N_4O_{12}Cu_2$
Formula weight = 711
Triclinic
Space group $P\bar{1}$
a = 8.033(5) A
b = 9.056(5) A
c = 11.013(5) A
α = 96.76(3)°
β = 103.65(3)°
γ = 111.52(3)°
D_c = 1.67 g cm^{-3}

Z = 1 (the compound is a dimer)
λ(Mo Kα) = 0.7107 A
μ(Mo Kα) = 52.9 cm^{-1}
Scan method = $\theta/2\theta$
Scan speed = 2° min^{-1}
Max. 2θ = 50°
Min. 2θ = 2°
Total reflexions = 2480
Observed reflexions = 1865
Criterion for observed refl $I > 3\sigma(I)$

TABLE II. Atomic Parameters for $[Cu(PDCNO)(py)(MeOH)]_2$

Atom	x/a	y/b	z/c
Atomic coordinates			
Cu1	0.1024(2)	0.3807(1)	0.2932(1)
O1	−0.0456(9)	0.4861(8)	0.3463(5)
O2	0.2034(8)	0.3858(8)	0.4748(5)
O3	−0.0750(9)	0.1720(8)	0.4430(6)
O4	−0.0543(9)	0.3270(8)	0.1170(5)
O5	−0.2801(10)	0.3314(9)	−0.0393(6)
N1	0.2418(10)	0.2521(9)	0.2442(6)
N2	−0.1145(9)	0.5744(8)	0.2771(6)
C1	0.4302(13)	0.3103(13)	0.3000(9)
C2	0.5290(16)	0.2189(16)	0.2728(11)
C3	0.4383(18)	0.0731(16)	0.1878(11)
C4	0.2456(19)	0.0164(15)	0.1319(10)
C5	0.1576(15)	0.1120(13)	0.1634(9)
C6	−0.1739(12)	0.5310(11)	0.1448(7)
C7	−0.2457(13)	0.6311(12)	0.0831(8)
C8	−0.2577(14)	0.7623(12)	0.1479(9)
C9	−0.1934(13)	0.8019(12)	0.2832(9)
C10	−0.1271(12)	0.6978(11)	0.3431(7)
C11	0.0708(13)	0.2771(12)	0.5103(8)
C12	−0.1682(12)	0.3873(11)	0.0691(8)
C13	0.3828(18)	0.7645(16)	0.3786(11)
O6	0.3216(11)	0.6247(9)	0.2844(6)
H1	0.5028	0.4279	0.3661
H2	0.6781	0.2644	0.3195
H3	0.5140	0.0023	0.1647
H4	0.1676	−0.1003	0.0651
H5	0.0085	0.0694	0.1180
H7	−0.2963	0.6008	−0.0204
H8	−0.3144	0.8359	0.0962
H9	−0.1954	0.9077	0.3384
H131	0.3043	0.8372	0.3548
H132	0.5260	0.8374	0.3907
H133	0.3640	0.7300	0.4663

(continued)

TABLE II. *(continued)*

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal parameters[a] ($U_{i,j} \times 10^{-4}$)						
Cu1	370(6)	488(7)	232(5)	92(4)	125(4)	218(5)
O1	558(41)	540(41)	294(33)	180(30)	192(30)	366(35)
O2	289(33)	584(42)	251(31)	112(29)	98(26)	128(31)
O3	511(45)	542(45)	372(39)	53(34)	78(34)	144(38)
O4	423(39)	634(47)	292(33)	43(31)	76(29)	253(36)
O5	596(47)	740(52)	263(35)	84(34)	31(32)	296(41)
N1	369(44)	463(47)	255(38)	86(35)	104(33)	181(38)
N2	297(38)	398(43)	290(37)	87(32)	127(30)	158(34)
C1	416(58)	620(68)	379(53)	174(49)	134(44)	202(52)
C2	489(66)	853(92)	671(78)	368(72)	314(59)	377(66)
C3	830(90)	912(95)	536(69)	271(68)	366(66)	654(81)
C4	871(95)	674(81)	465(66)	86(58)	114(63)	469(74)
C5	524(63)	579(68)	418(57)	36(51)	102(48)	285(55)
C6	329(49)	538(59)	234(43)	138(41)	148(37)	158(44)
C7	461(57)	629(68)	319(49)	223(47)	190(43)	262(52)
C8	495(61)	531(63)	435(56)	197(48)	201(47)	249(51)
C9	474(57)	459(56)	410(52)	155(44)	199(44)	273(48)
C10	336(48)	519(57)	239(44)	165(41)	146(37)	153(43)
C11	483(59)	489(58)	223(44)	63(42)	104(42)	285(51)
C12	374(52)	503(59)	273(47)	104(42)	132(41)	137(46)
C13	717(85)	682(83)	591(75)	147(64)	273(65)	103(68)
O6	813(58)	622(51)	417(42)	161(38)	272(40)	139(44)

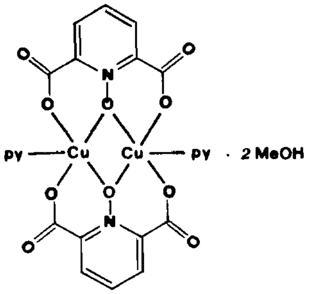
[a] Anisotropic thermal parameters are in the form $T = \exp 2\pi^2(U_{ij}H_iH_jA_i^*A_j^*)$.

TABLE III. Bond Distances and Angles for [Cu(PDCNO)(py)(MeOH)]$_2$

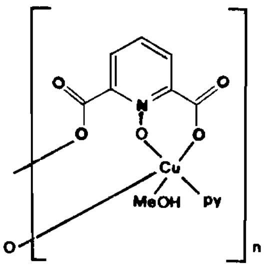
Distances (A)			
Cu–O(1)	1.923(7)	N(2)–C(6)	1.38(1)
Cu–O(2)	1.962(7)	C(6)–C(7)	1.40(1)
Cu–O(4)	1.941(7)	C(7)–C(8)	1.38(2)
Cu–N(1)	2.002(9)	C(8)–C(9)	1.42(2)
Cu–O(6)	2.298(9)	C(9)–C(10)	1.41(1)
N(1)–C(1)	1.37(1)	C(10)–N(2)	1.30(1)
C(1)–C(2)	1.41(2)	C(10)–C(11)	1.54(1)
C(2)–C(3)	1.38(2)	C(11)–O(2)	1.33(1)
C(3)–C(4)	1.41(2)	C(11)–O(3)	1.20(1)
C(4)–C(5)	1.39(2)	C(6)–C(12)	1.49(2)
C(5)–N(1)	1.30(1)	C(12)–O(4)	1.28(1)
N(2)–O(1)	1.34(1)	C(12)–O(5)	1.23(1)
		C(13)–O(6)	1.40(2)
Angles (deg)			
O(1)–Cu–O(2)	87.0(3)	C(10)–C(11)–O(2)	110.6(8)
O(1)–Cu–O(4)	89.9(3)	C(10)–C(11)–O(3)	127.9(8)
N(1)–Cu–O(2)	90.7(3)	O(2)–C(11)–O(3)	127.9(8)
N(1)–Cu–O(4)	91.0(3)	C(6)–C(12)–O(4)	110.6(8)
Cu–O(1)–N(2)	123.2(6)	C(6)–C(12)–O(5)	115.9(9)
Cu–O(2)–C(11)	108.7(6)	O(4)–C(12)–O(5)	123(1)
Cu–O(4)–C(12)	127.8(7)	Cu–O(6)–C(13)	121.8(8)

Discussion

The elemental analysis agrees with the formulation Cu(PDCNO)·py·MeOH, for which the structure **A** or **B** can be suggested.



A



B

If **B** were the correct arrangement the value of *n* should be small owing to the solubility of the complex in methanol. A binuclear structure of the type **B** was found in uranyl(VI) complexes with the same ligand [10, 11].

Infrared spectra cannot discriminate between the two configurations as the absorption bands associated with the carboxylate groups are expected to be almost

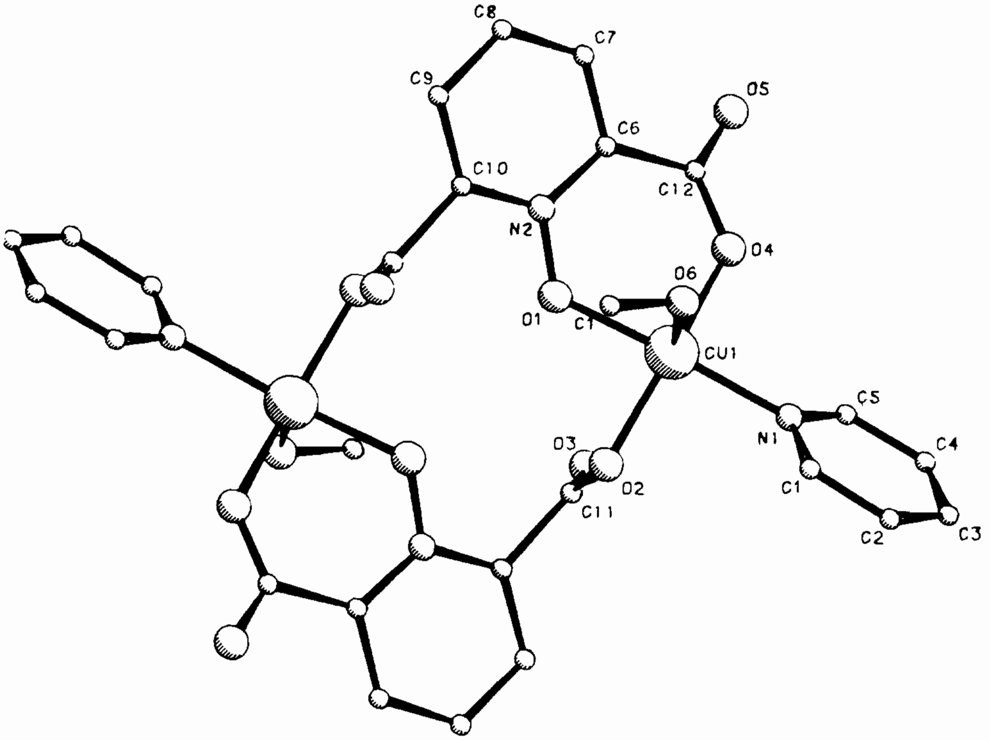


Fig. 1. The crystal structure of [Cu(PDCNO)(py)(MeOH)]$_2$.

at the same frequency with a comparable intensity for **A** and **B**. The stretching bands of the carboxylate groups of Cu(PDCNO)(py)(MeOH) lie at 1645 cm^{-1} (ν_{asymm}(COO)) and at 1360 cm^{-1} (ν_{symm}(COO)); the marked difference in the intensity of these two bands indicates that the carboxylate groups coordinate as monodentate and that a considerable delocalization of the double bond does not occur. It must be noted that in the free ligand the stretching frequencies associated to the C=O groups lie at 1755 and 1713 cm^{-1} while in the sodium salt of pyridine-2,6-dicarboxylate-*N*-oxide the ν_{asymm}(COO) was found at 1625 cm^{-1} and the ν_{symm}(COO) at 1376 cm^{-1}. The ν(N–O) was found in the copper complex at 1186 cm^{-1}, 42 cm^{-1} lower than found in the sodium salt; this indicates that the N–O group is coordinated to the copper(II) ion.

In the free ligand, where the N–O group is involved in hydrogen bonding with the carboxylic groups, the ν(N–O) lies at 1165 cm^{-1}.

Magnetic data, on the contrary, can give useful informations about the structure adopted by the complex.

The magnetic moment of 2.70 BM at room temperature (1.9 BM per copper atom) is normal and strongly supports structure **B** which is confirmed by the X-ray analysis.

As shown in Fig. 1, the structure consists of dimeric [Cu(PDCNO)(py)(MeOH)]$_2$ molecules, where the anions provide bridging of two crystallographic asymmetric units through the inversion centre at the origin of the cell.

The copper atoms are five-coordinated in the square pyramidal coordination geometry: the four nearest atoms around the metal ions, three (PDCNO) O atoms and the pyridine N atom, are arranged in a nearly-square-planar coordination, the fifth coordination site being occupied by the methanol oxygen, with a Cu–O distance of 2.30(1) Å. The in-plane Cu–O bond distances are comparable, irrespective of the fact that O(1) is not a carboxylic oxygen, while the out-of-plane Cu–O (methanol) distance is significantly longer, as expected. The metal is displaced by 0.18 Å from the base plane defined by O(1), O(2), O(4) and N(1). The equation of the plane is $0.455X + 0.890Y - 0.025Z = 1.421$ Å, where X, Y, Z are orthogonalized atomic coordinates, and deviations of the atoms from the plane are: O(1) 0.08, O(2) –0.07, O(4) –0.08, N(1) 0.09.

Structural details in the carboxylato groups are normal, C–O bonds concerning coordinated oxygen atoms being significantly longer than the carbonylic ones. The N–O bond distance of 1.34(1) Å compares well with 1.35 Å found in pyridine 1-oxide [13], so that this bond seems to be unaffected upon coordination.

Intermolecular linking of the modulo unit with adjacent molecules is provided by hydrogen bonding between the O(6) methanol oxygen and the O(5) carboxylato oxygen at x, $1-y$, z (O•••O = 2.74 Å). Other O•••O contacts in the structure are longer than 3 Å.

Acknowledgement

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