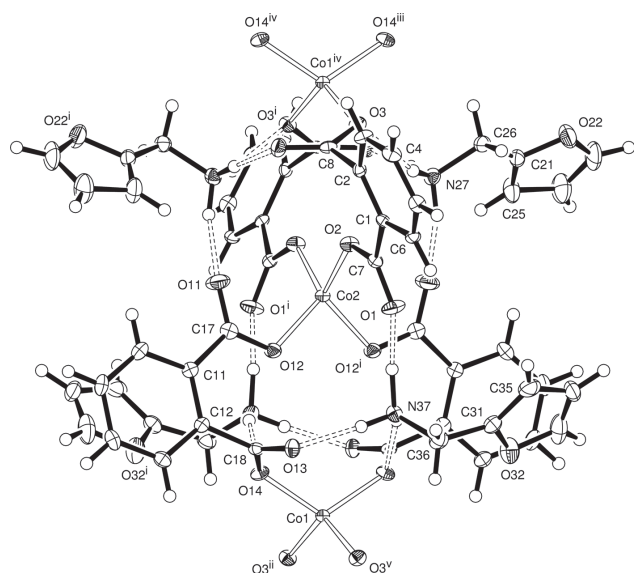


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Synthesis and crystal structure of bis(furan-2-ylmethanaminium)-catena-[bis(μ_2 -phthalato- κ^2 O:O')cobalt(II)], $C_{26}H_{24}CoN_2O_{10}$



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Abstract

$C_{26}H_{24}CoN_2O_{10}$, monoclinic, $F2/d$ (equiv. to no. 15), $a = 23.7125(7)$ Å, $b = 10.7325(4)$ Å, $c = 39.5740(15)$ Å, $\beta = 90.324(3)^\circ$, $V = 10071.2(6)$ Å³, $Z = 16$, $R_{gt}(F) = 0.0514$, $wR_{ref}(F^2) = 0.1048$, $T = 140(1)$ K.

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Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Prism., purple
Size:	$0.24 \times 0.09 \times 0.05$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.75 mm^{-1}
Diffractometer, scan mode:	Xcalibur 3/Sapphire3, φ and ω -scans
θ_{max} , completeness:	29.9° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	50446, 7337, 0.096
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 4968
$N(\text{param})_{\text{refined}}$:	377
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], ORTEPII [4], WinGX and ORTEP [5]

Source of materials

The title compound was prepared from a mixture of cobalt chloride, phthalic acid and furfurylamine in equal proportions. Suitable crystals were grown by slow evaporation of the solvent, $CHCl_3$.

Cobalt(II) chloride (2.38 g, 10 mmol) in 30 mL of ethanol was added gradually to the ethanolic solution of phthalic acid (PA) (1.22 g, 10 mmol), and furfurylamine (FA) ligand (1.66 g, 10 mmol), in the molar ratio 1:1:1 ($CoCl_2$:PA:FA) under continuous stirring. The mixture was kept undisturbed and irradiated at a stable medium power level (600 W) in a microwave oven. The precipitated solid complexes were filtered, washed several times with 50% (v/v) ethanol–water to remove any traces of unreacted starting materials. A purple colored compound was then separated out. The synthesized complexes were found to be highly soluble in DMSO and DMF and slightly soluble in $CHCl_3$. The evaporation of solvent yielded good quality crystals which were dried in a vacuum desiccator over anhydrous $CaCl_2$. Yield 65%, Mol. wt. 583.40, M.p. >300 °C. UV-Vis (DMSO) cm^{-1} , 12, 668–12,923, 15,374–15,758, 22,333–22,827, IR (KBr, cm^{-1}): 3475 (N–H), 2987 (C–H), 1725 (C=O), 1396 (C–N), 1083 (NH_2), 851, 728; Far IR (CsI, cm^{-1}) 445 (Co–O). ¹H NMR (300 MHz, δ p.p.m. from TMS in $CDCl_3$, 300 K): δ 9.97 (1H, br N–H, FA), δ 7.37–8.77 (8H, phenyl ring), δ 2.90 (2H, HN–CH₂). ¹³C NMR ($CDCl_3$) (δ , p.p.m.): 169–176 (4 C=O, 2 phenyl ring), 130–153 (phenyl ring 8 C), 130–137 (aromatic 5 C), 42 (CH₂). Molar conductance, Λ_m ($\Omega^{-1}cm^{-1}mol^{-1}$, 10^{-3} DMSO, r.t.): 16.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Co1	0.1250	0.05415(4)	0.3750	0.01133(11)
O1	0.24728(7)	0.53498(15)	0.34884(5)	0.0241(4)
O2	0.18789(6)	0.68087(14)	0.36767(5)	0.0165(4)
O3	0.19255(6)	0.95690(14)	0.36320(4)	0.0163(4)
O4	0.20981(7)	0.90369(15)	0.41709(5)	0.0196(4)
C1	0.28453(9)	0.7346(2)	0.36133(6)	0.0118(5)
C2	0.27795(9)	0.8526(2)	0.37562(6)	0.0131(5)
C3	0.32501(9)	0.9282(2)	0.38051(7)	0.0174(5)
H3	0.3207	1.0061	0.3905	0.021*
C4	0.37794(9)	0.8889(2)	0.37076(7)	0.0184(5)
H4	0.4092	0.9396	0.3745	0.022*
C5	0.38446(9)	0.7735(2)	0.35529(7)	0.0171(5)
H5	0.4199	0.7475	0.3482	0.020*
C6	0.33781(9)	0.6976(2)	0.35060(6)	0.0139(5)
H6	0.3421	0.6206	0.3401	0.017*
C7	0.23644(9)	0.6425(2)	0.35870(6)	0.0138(5)
C8	0.22204(9)	0.9049(2)	0.38693(7)	0.0141(5)
Co2	0.1250	0.56179(4)	0.3750	0.01183(11)
O11	0.14462(8)	0.59314(15)	0.44599(5)	0.0322(5)
O12	0.14189(6)	0.43534(14)	0.40997(4)	0.0175(4)
O13	0.22072(6)	0.20984(15)	0.40993(4)	0.0175(4)
O14	0.13054(6)	0.15258(14)	0.41659(4)	0.0158(4)
C11	0.16462(9)	0.3907(2)	0.46715(6)	0.0148(5)
C12	0.17441(9)	0.2638(2)	0.46112(6)	0.0137(5)
C13	0.18452(9)	0.1842(2)	0.48830(7)	0.0173(5)
H13	0.1898	0.0996	0.4844	0.021*
C14	0.18687(10)	0.2291(2)	0.52088(7)	0.0203(5)
H14	0.1934	0.1749	0.5388	0.024*
C15	0.17944(10)	0.3558(2)	0.52693(7)	0.0212(6)
H15	0.1821	0.3871	0.5488	0.025*
C16	0.16811(10)	0.4341(2)	0.50029(7)	0.0197(5)
H16	0.1626	0.5185	0.5045	0.024*
C17	0.14975(9)	0.4808(2)	0.43951(7)	0.0176(5)
C18	0.17642(9)	0.2081(2)	0.42621(6)	0.0138(5)
C21	0.11893(10)	0.8790(2)	0.24804(7)	0.0199(5)
O22	0.13348(8)	0.92978(17)	0.21765(5)	0.0317(5)
C23	0.09471(13)	0.8845(3)	0.19479(8)	0.0386(8)
H23	0.0943	0.9041	0.1719	0.046*
C24	0.05796(13)	0.8093(3)	0.20961(8)	0.0403(8)
H24	0.0280	0.7677	0.1994	0.048*
C25	0.07376(11)	0.8052(3)	0.24450(7)	0.0307(7)
H25	0.0561	0.7599	0.2615	0.037*
C26	0.15667(10)	0.9122(2)	0.27670(7)	0.0191(5)
H26A	0.1956	0.8964	0.2706	0.023*
H26B	0.1528	1.0001	0.2819	0.023*
N27	0.14159(10)	0.8368(2)	0.30671(6)	0.0179(5)
C31	0.25633(10)	0.2648(2)	0.28600(7)	0.0197(5)
O32	0.21454(7)	0.20441(17)	0.26820(5)	0.0298(5)
C33	0.21459(12)	0.2541(3)	0.23657(8)	0.0381(8)
H33	0.1904	0.2302	0.2192	0.046*
C34	0.25402(13)	0.3417(3)	0.23400(8)	0.0367(8)
H34	0.2620	0.3892	0.2150	0.044*
C35	0.28198(12)	0.3488(2)	0.26626(8)	0.0328(7)
H35	0.3118	0.4009	0.2722	0.039*
C36	0.26265(10)	0.2285(2)	0.32183(7)	0.0223(6)

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
H36A	0.3000	0.2518	0.3297	0.027*
H36B	0.2592	0.1387	0.3237	0.027*
N37	0.21944(9)	0.28909(19)	0.34365(6)	0.0163(4)
H27A	0.1640(11)	0.850(2)	0.3226(8)	0.025(8)*
H27B	0.1384(13)	0.749(3)	0.3035(9)	0.066(11)*
H27C	0.1067(12)	0.861(3)	0.3149(8)	0.035(8)*
H37A	0.2206(10)	0.257(2)	0.3665(7)	0.022(7)*
H37B	0.2255(12)	0.3724(17)	0.3460(8)	0.053(10)*
H37C	0.1844(13)	0.272(3)	0.3369(8)	0.044(9)*

Experimental crystallographic details

The space group *F2/d* is a non-standard setting of *C2/c* (no. 15). This was derived from the diffractometer-generated *I*-centred cell with $\beta = 118.141^\circ$; application of the transformation matrix: $101/0-10/10-1$, yielded the more appropriate cell with $\beta = 90.324^\circ$. The ammonium hydrogen atoms were located in difference maps and were refined freely, except for H(37b) for which the N(37)–H(37b) bond was restrained to 0.87(2) Å. The remaining hydrogen atoms were included in idealised positions (C–H distances set to 0.93 Å) and their *U*_{iso} values were set to ride on the *U*_{eq} values of the parent carbon atoms.

Comment

Transition metal complexes have been among the most widely studied coordination compounds in recent years because they are becoming progressively more significant as biochemical, analytical and antimicrobial reagents [6, 7]. The complexes containing metal ions are active in many biological processes and show immense biological activity such as allied with certain metal-proteins, complexes contributing in oxygen transport, electronic transfer reactions or the storage of ions [8, 9] and have generated massive interest in the study of systems containing these metals [10]. Metal-based drugs have achieved much significance in medicinal fields and are used as medicines for the treatment of diabetes, cancer, anti-inflammatory and cardiovascular disease [11–13].

The crystals analysed show a coordination polymer, [Co{C₆H₄(COO)₂}]_n, 2n(C₄H₃OCH₂NH₃), a portion of which is shown by the Figure; symmetry codes are: (i) $1/4-x, y, 3/4-z$; (ii) $1/4-x, y-1, 3/4-z$; (iii) $1/4-x, 1+y, 3/4-z$; (iv) $x, 1+y, z$; (v) $x, y-1, z$. Each cobalt atom is four-coordinate with a tetrahedral pattern. The cobalt atoms are bridged by pairs of phthalate ions (related by twofold symmetry axes) and are linked in a polymeric chain parallel to the *b* axis; the repeating unit, r.u., is from Co(1) to Co(1^{iv}).

The phthalate ligand has been shown to be versatile and flexible and able to coordinate metal atoms in a wide variety

of patterns. In our sample, a pair of phthalate ligands bind two cobalt ions in a 14-membered ring, with the cobalt ligands 5.448 and 5.284 Å apart, as shown in the Figure. The 14-membered ring is common in metal-phthalate complexes, but is normally formed about a centre of symmetry, in contrast to the two-fold symmetry shown in this structure. Furthermore, this coordination polymer is formed by a chain of $-Co-(phthalate)_2-Co-$ units along the two-fold symmetry axis, and we believe that this is a novel pattern in a phthalate polymer chain. We have, however, noted coordination polymers showing some similar features in complexes of substituted phthalates with copper [14] and zinc [15].

There are two distinct furfurylammonium cations in the title structure. They differ in the orientation of the $C-NH_3$ groups with respect to the furan ring. They lie separate from the $Co\{C_6H_4(COO)_2\}_2$ polymer chains but the aminium hydrogen atoms all form classical hydrogen bonds to the carboxylate oxygen atoms. There are no hydrogen bonds between the r.u. and the adjacent units along the chain, and there are no hydrogen bonds between the chains.

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