Crystal and molecular structure of the solvate of bis(2,6-bis(1′-methylbenzimidazol-2′-yl)pyridine)cobalt(II) dihexafluorophosphate with 4-methyl-1,3-dioxolan-2-on

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Abstract

The crystal structure of $[(CoL_2)(PF_6)_2]\cdot 3(C_4H_6O_3)$ (I) (L = 2,6-bis(1′-methylbenzimidazol-2′-yl)pyridine, $C_{21}H_{17}N_5$) at 250 K was determined by single crystal X-ray diffraction ($R = 0.109$ for 8411 reflections with $F > 4\sigma(F)$). The crystal includes all three components $(CoL_2)^{2+}$, PF_6^- and the electrolyte $C_4H_6O_3$ for the corresponding redox system $(CoL_2)^{2+}/(CoL_2)^{3+}$ used in new photovoltaic cells based on nanocrystalline TiO_2 films. Two symmetrically independent cations $(CoL_2)^{2+}$ (**Ia** and **Ib**) have a very similar geometry; every Co(II) atom is hexacoordinated by six N atoms of two mutually perpendicular neutral L ligands. The coordination polyhedron of the Co(II) atoms can be described as a flattened tetrahedron formed by four Co–N(benzimidazol) bonds (av. Co–N distance of 2.121 Å) with two pseudo-axial Co–N(pyridine) bonds (av. Co–N distance of 2.077 Å). The cations **Ia** and **Ib** are arranged in the crystal of **I** in two independent infinite chains extending along the screw axes 2_1, with the formation of sheets parallel to the (101) plane. The PF_6^- anions and the solvent molecules 4-methyl-1,3-dioxolan-2-on are located in the spaces between the sheets. The instability of crystals of **I** in air is explained by the loss of solvent.

Key words: Crystal structures; Cobalt complexes; Pyridine derivative complexes; Chelating ligand complexes

Introduction

In the course of a systematic study of the structure and morphology of thin metal oxide films for a new type of photovoltaic system for solar light harvesting and conversion to electricity [1, 2], scanning electron microscopy and X-ray powder diffraction studies of the multilayered films were performed. The dependence of the morphology of the films on the conditions of their preparation was discussed (e.g. on the temperature of thermal treatment and the density of current for electrochemically obtained films). The top layer of the films is formed by nanocrystalline colloidal TiO_2 particles [3]. We report here the crystal and molecular structure at 250 K of bis(2,6-bis(1′-methylbenzimidazol-2′-yl)-pyridine)cobalt(II) dihexafluorophosphate $(CoL_2)^{2+}$-$(PF_6)_2^-$ crystallized as a solvate **I** with 4-methyl-1,3-dioxolan-2-on. All the components (CoL_2^{2+} cations, PF_6^- anions and 4-methyl-1,3-dioxolan-2-on) are parts of the redox system $(CoL_2)^{2+}/(CoL_2)^{3+}$ in the electrolyte, which separates the sensitiser layer on the surface of the TiO_2 film from the $SnO_{2-x}F_x$ counter electrode in a photovoltaic cell with transparent glass electrodes [1]. Before this, only the crystal structure of the Cu(II) complex of ligand L was known [4]. On the basis of magnetic and spectroscopic studies of Fe(II)

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complexes with the ligand L the metal-to-ligand charge transfer in the FeN_6 chromophore was suggested as an explanation for the observed strong absorption in the 550 nm region and the onset of the spin transition near 313 K [5]. In principle, the detailed analysis of the geometry of the Co(II) coordination using X-ray data may help in an assignment of the spin-state of this complex, because the spin-state transitions in metal complexes (which are driven by a change of temperature or pressure) are always associated with a considerable reorganization of molecular geometry [6]. The structure of the Fe(II) complex with a non-N-methylated ligand (bzimpy) was studied as well [7].

The aims of the present X-ray study were the elucidation of the coordination of the Co(II) atoms, the geometry of the N-donor ligands, and the investigation of the crystal packing in the mixed crystal **I** in relation to the function of the corresponding redox system in the photovoltaic cell. The possible mechanism of action in the redox system $(CoL_2)^{2+}/(CoL_2)^{3+}$ in solar cells is discussed in more detail in ref. 8. The spectroscopic and magnetic properties of the complex $(CoL_2)^{2+}$ will be reported later.

Experimental

Preparation

The ligand 2,6-bis(1′-methylbenzimidazol-2′-yl)-pyridine (L) was synthesized according to ref. 5. A solution of $CoCl_2$ (0.25 g, 1.05 mmol) in water was added dropwise to an ethanol solution (0.71 g, 2.11 mmol) of the ligand, and the solution turned yellow immediately. Then the compound $(CoL_2)(PF_6)_2$ was precipitated by addition of an aqueous saturated potassium hexafluorophosphate (KPF_6) solution. The compound was filtered, washed thoroughly with water and ether, and dried under vacuum. The powder of $(CoL_2)(PF_6)_2$ was dissolved in an acetonitrile and 4-methyl-1,3-dioxolan-2-on mixture (2:1). Upon standing at room temperature for some weeks large good-faced prismatic crystals of **I** were formed.

TABLE 1. Experimental details of X-ray structure determination

Empirical formula	$C_{54}H_{52}CoF_{12}N_{10}O_9P_2$		
Formula weight	1315.8		
Crystal colour, habit	orange, prism		
Crystal dimensions (mm)	0.27×0.30×0.30		
Crystal system	monoclinic		
Lattice parameters	250 K	170 K	293 K
a (Å)	15.629(7)	15.514(4)	15.75(1)
b (Å)	18.563(6)	18.486(4)	18.62(2)
c (Å)	19.990(6)	19.754(6)	20.14(2)
β (°)	90.11(3)	90.26(2)	90.07(7)
V (Å^3)	5800	5665.3	5792.2
Space group	$P2_1$		
Z		4	
Density (calc.) (Mg m^{-3})	1.507		
Absorption coefficient (mm^{-1})	0.447		
F(000)	2660		
Radiation	Mo Kα		
T (K)	250		
2θ Range (°)	4.0–54.0		
Scan type	$\omega/2\theta$		
Reflections collected	13608		
Independent reflections	13123		
Observed reflections	8411 ($F > 4.0\sigma(F)$)		
Structure solution	direct methods (SHELXTL PLUS)		
Refinement method	full-matrix least-squares		
Function minimized	$\Sigma w(F_o - F_c)^2$		
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.01F^2$		
Hydrogen atoms	riding model, fixed U_{iso}		
No. parameters	1464		
Residuals R, R_w	0.109, 0.128		
Reflection/parameter ratio	5.7:1		
Goodness of fit	1.29		
Largest residual electron density (e Å^{-3})	1.13		

X-ray single crystal study

Diffraction data on crystals of **I** were collected at 250 K on the Siemens R3/m four circle X-ray diffractometer using Mo Kα radiation with a graphite monochromator. The lattice parameters were refined with 24 centred reflections with 2θ values between 22 and 24°. The $\omega/2\theta$ scan technique to $2\theta_{\max}=54°$ was used to record the intensities of 13 608 reflections. Three reflections were monitored every 100 reflections to check the crystal decomposition. Correction for crystal decay during the measurement (due to loss of solvent) was applied. There was a maximal drop of intensities of standard reflections of about 18%. (A first attempt to refine the structure with the room temperature data was unsuccessful.) There were no reflections with essential intensities at 2θ angles higher than 54° (indicating a considerable librational or rotational disorder or a mobility). The rotation photographs along all three axes, a symmetry test of the XPREP program and the non-centrosymmetrical statistics of reflections indicated the space group $P2_1$ with two symmetrically independent formula units $(CoL_2)^+(PF_6)_2^-$. The monoclinic angle is near to 90°. The structure was solved by direct methods and refined by full-matrix least-squares to $R=0.109$ ($R_w=0.128$) with anisotropic approximation of the thermal movement of all non-hydrogen atoms except the fluorine atoms of the PF_6^- anions. An attempt to solve the structure in the centrosymmetric space group $P2_1/m$ with one symmetrically independent formula per unit cell was unsuccessful. In the course of the refinement six symmetrically independent solvent molecules of 4-methyl-1,3-dioxolan-4-on were found. The hydrogen atoms, whose positions were reassigned geometrically at every stage of the refinement, were included in the calculation of structure factors but not refined. The hydrogen atoms of the solvent molecules were not included in the calculations (172 non-hydrogen atoms, 1464 refined parameters). No absorption correction was applied ($\mu=0.447$ mm^{-1}). The crystallographic data for **I** are given in Table 1 (the unit cell parameters of **I** were determined also at 270 K on the Syntex P2$_1$ four circle diffractometer and at 170 K on the Stoe Imaging Plate Diffraction System). The positional and equivalent isotropic parameters are listed in Table 2, the relevant bond lengths and angles are collected in Table 3, and the equations of planar moieties in the cations of **I** are given in Table 4.

The structure of cations is shown in Fig. 1, the cation numbering scheme is explained in Fig. 2, and the crystal packing is shown in Figs. 3 and 4. All calculations were performed on a VAX 3100 station using the SHELXTL-PLUS program package [9].

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **I**

	x	y	z	U_{eq}^{a}
Co(1)	566(1)	4367	613(1)	22(1)
N(101)	31(6)	3362(5)	925(5)	27(1)
N(102)	−601(6)	4650(5)	1022(5)	24(1)
N(103)	540(7)	5503(5)	523(5)	30(1)
N(104)	−127(7)	6538(6)	793(6)	37(1)
N(105)	−1028(7)	2734(6)	1354(5)	33(1)
N(201)	1464(6)	4388(6)	1392(5)	27(1)
N(202)	1709(6)	4105(5)	141(5)	26(1)
N(203)	199(6)	4180(5)	−398(5)	30(1)
N(204)	581(7)	4014(6)	−1456(5)	32(1)
N(205)	2835(7)	4256(7)	1729(6)	43(1)
C(101)	1844(8)	6076(7)	41(7)	42(1)
C(102)	2248(8)	6755(8)	−70(8)	49(1)
C(103)	1844(10)	7361(8)	139(8)	54(1)
C(104)	1063(9)	7390(8)	403(8)	50(1)
C(105)	675(9)	6722(7)	519(7)	40(1)
C(106)	1059(8)	6067(7)	348(6)	33(1)
C(107)	−778(10)	7050(8)	1009(9)	67(1)
C(108)	−176(7)	5793(6)	788(6)	27(1)
C(109)	−851(8)	5336(7)	1009(7)	35(1)
C(110)	−1674(8)	5526(8)	1207(8)	51(1)
C(111)	−2239(9)	4993(9)	1369(9)	69(1)
C(112)	−1965(8)	4274(8)	1387(8)	53(1)
C(113)	−1152(7)	4109(6)	1209(6)	26(1)
C(114)	−735(7)	3401(6)	1173(6)	27(1)
C(115)	279(8)	2653(7)	935(6)	31(1)
C(116)	1013(8)	2310(6)	723(7)	35(1)
C(117)	1078(10)	1549(7)	810(8)	53(1)
C(118)	391(9)	1190(7)	1101(7)	49(1)
C(119)	−397(10)	1502(7)	1279(7)	51(1)
C(120)	−422(8)	2240(6)	1220(6)	31(1)
C(121)	−1879(9)	2551(8)	1621(8)	55(1)
C(201)	−1366(8)	4412(7)	−640(7)	40(1)
C(202)	−1955(8)	4464(9)	−1133(7)	50(1)
C(203)	−1671(10)	4346(10)	−1823(9)	72(1)
C(204)	−895(9)	4222(8)	−1975(7)	50(1)
C(205)	−290(8)	4173(7)	−1465(6)	35(1)
C(206)	−539(8)	4260(6)	−787(6)	29(1)
C(207)	1110(9)	3889(9)	−2064(7)	54(1)
C(208)	822(8)	4053(6)	−816(6)	30(1)
C(209)	1716(8)	3945(6)	−515(6)	31(1)
C(210)	2427(8)	3699(8)	−825(7)	45(1)
C(211)	3165(10)	3636(10)	−476(8)	63(1)
C(212)	3160(9)	3779(9)	218(8)	55(1)
C(213)	2392(8)	4025(6)	513(6)	31(1)
C(214)	2248(7)	4200(6)	1227(6)	31(1)
C(215)	1508(8)	4556(7)	2078(6)	33(1)
C(216)	874(9)	4770(8)	2503(7)	50(1)
C(217)	1171(10)	4969(9)	3154(7)	60(1)
C(218)	1981(10)	4873(9)	3353(7)	63(1)
C(219)	2585(10)	4660(10)	2920(8)	67(1)
C(220)	2352(8)	4482(7)	2300(7)	43(1)
C(221)	3749(10)	4140(11)	1741(10)	98(1)
Co(2)	4167(1)	3256(1)	4544(1)	24(1)
N(301)	4415(6)	4263(5)	4072(5)	25(1)
N(302)	4994(6)	2997(5)	3760(5)	27(1)
N(303)	4296(7)	2118(6)	4608(5)	34(1)
N(304)	5180(7)	4881(6)	3314(5)	31(1)
N(305)	4772(7)	1104(5)	4146(6)	36(1)

(continued)

TABLE 2. (*continued*)

	x	y	z	U_{eq}[a]
N(401)	4992(7)	3440(5)	5367(5)	31(1)
N(402)	3342(6)	3569(5)	5299(5)	28(1)
N(403)	2928(6)	3153(6)	4126(5)	34(1)
N(404)	5166(8)	3656(6)	6453(6)	44(1)
N(405)	1507(7)	3382(6)	4212(6)	40(1)
C(301)	3693(8)	5351(7)	4585(7)	39(1)
C(302)	3644(9)	6082(8)	4523(8)	53(1)
C(303)	4137(11)	6476(7)	4054(9)	70(1)
C(304)	4675(10)	6133(8)	3617(9)	56(1)
C(305)	4706(8)	5391(7)	3689(7)	37(1)
C(306)	4209(7)	5003(6)	4163(6)	31(1)
C(307)	5806(9)	5073(8)	2802(8)	51(1)
C(308)	4990(7)	4233(7)	3583(6)	30(1)
C(309)	5271(7)	3521(7)	3354(6)	30(1)
C(310)	5768(10)	3359(7)	2772(8)	58(1)
C(311)	5929(10)	2659(8)	2634(8)	57(1)
C(312)	5650(10)	2107(8)	3099(8)	63(1)
C(313)	5174(8)	2308(6)	3626(6)	32(1)
C(314)	4775(8)	1840(6)	4137(6)	30(1)
C(315)	3928(8)	1550(6)	4950(6)	30(1)
C(316)	3365(8)	1552(7)	5487(7)	40(1)
C(317)	3114(9)	887(8)	5721(7)	49(1)
C(318)	3411(9)	264(8)	5469(8)	54(1)
C(319)	3998(9)	235(7)	4919(8)	50(1)
C(320)	4208(8)	918(7)	4680(6)	37(1)
C(321)	5314(11)	594(8)	3786(8)	67(1)
C(401)	6598(8)	3191(7)	5141(8)	45(1)
C(402)	7331(9)	3152(9)	5449(9)	61(1)
C(403)	7457(10)	3283(10)	6120(9)	68(1)
C(404)	6735(10)	3473(9)	6515(8)	56(1)
C(405)	5962(8)	3511(7)	6215(7)	38(1)
C(406)	5880(9)	3374(6)	5542(7)	39(1)
C(407)	4951(9)	3786(9)	7182(7)	57(1)
C(408)	4620(8)	3622(6)	5936(7)	35(1)
C(409)	3679(8)	3751(6)	5927(6)	34(1)
C(410)	3105(10)	4027(9)	6410(7)	60(1)
C(411)	2315(9)	4102(9)	6296(7)	57(1)
C(412)	1954(9)	3915(9)	5682(8)	59(1)
C(413)	2530(8)	3645(7)	5208(7)	38(1)
C(414)	2295(8)	3390(7)	4511(7)	41(1)
C(415)	2506(8)	2929(7)	3547(6)	36(1)
C(416)	2854(9)	2617(8)	2946(8)	51(1)
C(417)	2268(10)	2430(9)	2484(8)	67(1)
C(418)	1422(11)	2578(10)	2540(9)	80(1)
C(419)	1090(10)	2896(9)	3065(8)	62(1)
C(420)	1656(8)	3060(7)	3580(7)	41(1)
C(421)	701(9)	3660(11)	4471(9)	73(1)
F(11)	7965(13)	3000(13)	3186(12)	244(2)
F(12)	8745(11)	3380(11)	3984(10)	176(2)
F(13)	7575(10)	3842(10)	3894(9)	153(2)
F(14)	9005(12)	3750(12)	2897(11)	199(2)
F(15)	8897(12)	4345(13)	3711(12)	220(2)
F(16)	7723(13)	3981(12)	2802(11)	218(2)
P(2)	3155(3)	5496(2)	8061(2)	48(1)
F(21)	3140(9)	4662(8)	7936(8)	116(2)
F(22)	3273(10)	6301(9)	8182(8)	130(2)
F(23)	2861(11)	5605(11)	7289(9)	159(2)
F(24)	4115(8)	5480(7)	7785(6)	91(2)
F(25)	2211(8)	5488(8)	8315(7)	103(2)
F(26)	3493(8)	5352(8)	8779(7)	107(2)
P(3)	5845(3)	3606(4)	524(3)	83(1)
F(31)	5804(10)	4176(10)	1134(9)	156(2)
F(32)	6419(13)	3120(12)	965(12)	220(2)
F(33)	5211(13)	4172(13)	241(12)	223(2)
F(34)	6612(9)	4007(9)	255(8)	127(2)
F(35)	5075(9)	3205(9)	810(7)	117(2)
F(36)	5826(14)	3160(14)	−114(13)	284(2)
P(4)	3059(4)	2175(3)	7643(4)	90(1)
F(41)	2127(13)	2347(13)	7774(11)	222(2)
F(42)	2779(10)	1418(10)	7418(8)	137(2)
F(43)	3291(11)	2952(11)	7855(10)	179(2)
F(44)	3989(15)	1935(15)	7694(14)	341(2)
F(45)	3449(14)	2314(14)	6958(14)	311(2)
F(46)	2894(9)	2020(9)	8473(8)	131(2)
O(1S)	8981(8)	4949(8)	6425(7)	87(1)
O(2S)	9368(8)	4474(7)	5488(6)	75(1)
O(3S)	10091(9)	4182(10)	6367(8)	111(1)
C(1S)	9528(10)	4492(10)	6102(8)	64(1)
C(2S)	8308(11)	5171(10)	5927(9)	77(1)
C(3S)	8621(11)	4927(11)	5300(10)	85(1)
C(4S)	8094(15)	5962(15)	6097(15)	213(1)
O(4S)	6387(14)	1773(14)	7737(13)	232(1)
O(5S)	7066(10)	1042(9)	8304(8)	112(1)
O(6S)	5601(13)	726(12)	7976(11)	179(1)
C(5S)	6220(15)	1085(14)	8028(14)	160(1)
C(6S)	7814(13)	1469(13)	8014(12)	125(1)
C(7S)	7239(12)	2148(11)	7810(10)	90(1)
C(8S)	7096(16)	2715(16)	8403(16)	313(1)
O(10S)	3924(9)	−36(9)	1757(8)	103(1)
O(11S)	3851(11)	1017(11)	2296(10)	142(1)
O(12S)	3528(12)	98(12)	2888(11)	173(1)
C(13S)	3665(14)	322(13)	2340(13)	134(1)
C(14S)	4174(13)	386(13)	1253(12)	117(1)
C(15S)	3977(15)	1095(15)	1453(15)	203(1)
C(16S)	4464(16)	1650(16)	1478(16)	340(1)
O(7S)	8045(10)	1016(9)	4431(8)	105(1)
O(8S)	9471(11)	1006(11)	4297(10)	136(1)
O(9S)	8804(12)	384(12)	5113(11)	170(1)
C(9S)	8701(13)	783(12)	4645(11)	106(1)
C(10S)	8183(15)	1584(14)	3845(14)	173(1)
C(11S)	9009(12)	1515(12)	3804(11)	99(1)
C(12S)	9312(15)	1210(15)	3128(15)	211(1)
O(13S)	4080(11)	2142(11)	9611(9)	137(1)
O(14S)	3740(14)	985(14)	9655(13)	245(1)
O(15S)	2808(14)	1850(14)	10051(13)	256(1)
C(17S)	3407(16)	1412(16)	9750(16)	289(1)
P(1)	8313(3)	3835(4)	3408(3)	76(1)
C(18S)	4965(16)	1899(16)	9199(15)	278(1)
C(19S)	4760(15)	1093(15)	9273(15)	220(1)
C(20S)	5520(16)	828(16)	9594(16)	364(1)
O(16S)	−332(10)	2046(9)	6468(9)	114(1)
O(17S)	214(11)	1529(10)	7242(9)	127(1)
O(18S)	−641(10)	2351(10)	7783(9)	121(1)
C(21S)	−367(12)	2181(12)	7224(11)	99(1)
C(22S)	417(13)	1691(12)	6363(12)	117(1)
C(23S)	863(12)	1296(11)	6816(10)	88(1)
C(24S)	656(11)	1820(11)	5630(10)	82(1)

(*continued*)

[a] Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Relevant bond lengths (Å) and bond angles (°) for cations **Ia** and **Ib**

Bond lengths			
Co(1)–N(101)	2.138(10)	Co(1)–N(102)	2.069(9)
Co(1)–N(103)	2.118(10)	Co(1)–N(201)	2.094(9)
Co(1)–N(202)	2.080(10)	Co(1)–N(203)	2.129(10)
N(101)–C(114)	1.299(15)	N(101)–C(115)	1.373(15)
N(102)–C(109)	1.332(16)	N(102)–C(113)	1.375(15)
N(103)–C(106)	1.369(16)	N(103)–C(108)	1.351(15)
N(104)–C(105)	1.410(17)	N(104)–C(107)	1.459(19)
N(104)–C(108)	1.385(15)	N(105)–C(114)	1.367(16)
N(105)–C(120)	1.346(16)	N(105)–C(121)	1.473(18)
N(201)–C(214)	1.317(14)	N(201)–C(215)	1.409(15)
N(202)–C(209)	1.343(16)	N(202)–C(213)	1.309(15)
N(203)–C(206)	1.397(15)	N(203)–C(208)	1.304(16)
N(204)–C(205)	1.393(16)	N(204)–C(207)	1.489(17)
N(204)–C(208)	1.336(16)	N(205)–C(214)	1.364(16)
N(205)–C(220)	1.432(18)	N(205)–C(221)	1.445(19)
Co(2)–N(301)	2.130(10)	Co(2)–N(302)	2.089(10)
Co(2)–N(303)	2.125(11)	Co(2)–N(401)	2.117(10)
Co(2)–N(402)	2.069(10)	Co(2)–N(403)	2.117(10)
N(301)–C(306)	1.424(15)	N(301)–C(308)	1.330(15)
N(302)–C(309)	1.339(16)	N(302)–C(313)	1.337(15)
N(303)–C(314)	1.310(16)	N(303)–C(315)	1.382(16)
N(304)–C(305)	1.418(16)	N(304)–C(307)	1.463(18)
N(304)–C(308)	1.352(16)	N(305)–C(314)	1.368(15)
N(305)–C(320)	1.427(17)	N(305)–C(321)	1.461(19)
N(401)–C(406)	1.436(17)	N(401)–C(408)	1.321(17)
N(402)–C(409)	1.402(16)	N(402)–C(413)	1.290(16)
N(403)–C(414)	1.329(17)	N(403)–C(415)	1.396(17)
N(404)–C(405)	1.360(18)	N(404)–C(407)	1.514(18)
N(404)–C(408)	1.341(17)	N(405)–C(414)	1.368(17)
N(405)–C(420)	1.418(18)	N(405)–C(421)	1.458(18)
Bond angles			
N(101)–Co(1)–N(102)	76.2(4)	N(101)–Co(1)–N(103)	152.5(4)
N(102)–Co(1)–N(103)	76.3(4)	N(101)–Co(1)–N(201)	93.5(4)
N(102)–Co(1)–N(201)	107.0(4)	N(103)–Co(1)–N(201)	93.2(4)
N(101)–Co(1)–N(202)	105.4(4)	N(102)–Co(1)–N(202)	176.2(4)
N(103)–Co(1)–N(202)	102.2(4)	N(201)–Co(1)–N(202)	76.5(4)
N(101)–Co(1)–N(203)	91.7(4)	N(102)–Co(1)–N(203)	100.4(4)
N(103)–Co(1)–N(203)	94.4(4)	N(201)–Co(1)–N(203)	152.6(4)
N(202)–Co(1)–N(203)	76.2(4)	Co(1)–N(101)–C(114)	115.1(8)
Co(1)–N(101)–C(115)	136.9(8)	C(114)–N(101)–C(115)	107.9(10)
Co(1)–N(102)–C(109)	119.6(8)	Co(1)–N(102)–C(113)	118.3(7)
C(109)–N(102)–C(113)	121.3(10)	Co(1)–N(103)–C(106)	140.5(8)
Co(1)–N(103)–C(108)	112.2(7)	C(106)–N(103)–C(108)	106.8(10)
C(105)–N(104)–C(107)	125.3(11)	C(105)–N(104)–C(108)	106.8(10)
C(107)–N(104)–C(108)	127.8(11)	C(114)–N(105)–C(120)	109.1(10)
C(114)–N(105)–C(121)	127.4(11)	C(120)–N(105)–C(121)	123.4(11)
Co(1)–N(201)–C(214)	115.5(8)	Co(1)–N(201)–C(215)	139.4(8)
C(214)–N(201)–C(215)	105.0(9)	Co(1)–N(202)–C(209)	120.2(8)
Co(1)–N(202)–C(213)	117.9(8)	C(209)–N(202)–C(213)	121.5(10)
Co(1)–N(203)–C(206)	137.0(8)	Co(1)–N(203)–C(208)	115.9(8)
C(206)–N(203)–C(208)	106.2(10)	C(205)–N(204)–C(207)	124.5(10)
C(205)–N(204)–C(208)	105.9(10)	C(207)–N(204)–C(208)	129.4(11)
C(214)–N(205)–C(220)	104.8(10)	C(214)–N(205)–C(221)	131.6(13)
C(220)–N(205)–C(221)	123.6(12)	N(301)–Co(2)–N(302)	75.9(4)
N(301)–Co(2)–N(303)	151.9(4)	N(302)–Co(2)–N(303)	76.0(4)
N(301)–Co(2)–N(401)	95.3(4)	N(302)–Co(2)–N(401)	104.1(4)
N(303)–Co(2)–N(401)	93.2(4)	N(301)–Co(2)–N(402)	101.0(4)
N(302)–Co(2)–N(402)	176.8(4)	N(303)–Co(2)–N(402)	107.1(4)
N(401)–Co(2)–N(402)	76.5(4)	N(301)–Co(2)–N(403)	94.1(4)
N(302)–Co(2)–N(403)	104.5(4)	N(303)–Co(2)–N(403)	91.2(4)
N(401)–Co(2)–N(403)	151.3(4)	N(402)–Co(2)–N(403)	75.0(4)
Co(2)–N(301)–C(306)	138.5(8)	Co(2)–N(301)–C(308)	114.3(8)
C(306)–N(301)–C(308)	106.7(10)	Co(2)–N(302)–C(309)	119.3(8)
Co(2)–N(302)–C(313)	120.1(8)	C(309)–N(302)–C(313)	120.3(10)
Co(2)–N(303)–C(314)	113.7(8)	Co(2)–N(303)–C(315)	138.5(8)
C(314)–N(303)–C(315)	107.0(10)	C(305)–N(304)–C(307)	124.0(11)
C(305)–N(304)–C(308)	105.6(10)	C(307)–N(304)–C(308)	130.1(11)
C(314)–N(305)–C(320)	104.7(10)	C(314)–N(305)–C(321)	129.8(11)
C(320)–N(305)–C(321)	124.9(11)	Co(2)–N(401)–C(406)	139.7(8)
Co(2)–N(401)–C(408)	116.2(8)	C(406)–N(401)–C(408)	103.8(10)
Co(2)–N(402)–C(409)	119.2(8)	Co(2)–N(402)–C(413)	122.9(9)
C(409)–N(402)–C(413)	117.8(11)	Co(2)–N(403)–C(414)	115.0(9)
Co(2)–N(403)–C(415)	141.7(8)	C(414)–N(403)–C(415)	103.2(10)
C(405)–N(404)–C(407)	124.9(11)	C(405)–N(404)–C(408)	107.6(11)
C(407)–N(404)–C(408)	127.4(12)	C(414)–N(405)–C(420)	104.2(10)
C(414)–N(405)–C(421)	128.3(12)	C(420)–N(405)–C(421)	127.5(12)

X-ray powder study

Crystals of **I** were taken from the mother liquid, ground to a fine powder and divided into three batches (a), (b) and (c). Batch (a) was immediately sealed in a capillary with a small amount of mother liquid, batch (b) was left in air for one day and then sealed, and batch (c) was exposed to air for one week. X-ray powder patterns of all three batches were recorded using a STOE automatic powder diffractometer (Cu Kα radiation, Ge-monochromator, small linear position sensitive detector, data collection in Debye mode, 150 steps within 2θ interval of 4–80°, 1000 s per step). The full diffraction patterns of batches (a), (b) and (c) are shown in Table 5. A comparison of the powder diffraction patterns (Fig. 5) clearly indicates the change of the structure of **I** in air. TGA measurements show that this change is caused by the loss of solvent: crystals of **I** heated at 80 °C have lost 50% of the solvent after 20 h. Desolvation of compound **I** leads to destruction of the single crystal and thus does not allow for a single crystal structure study of the new desolvated phase. The redistribution of the intensities of some reflections is dramatic (see, for example, the peak (200), Table 5) which may explain the poor accuracy of our structure determination. The data collection at low temperature ($T = 250$ K) only partly delayed the desolvation.

Results and discussion

The crystal of phase **I** is built up of two symmetrically independent cations CoL^{2+} (**Ia** and **Ib**), four anions PF_6^- and six molecules of 4-methyl-1,3-dioxolan-2-on.

The cations **Ia** and **Ib** have a very similar geometry; every Co(II) atom is coordinated by six N atoms of two approximately planar mutually perpendicular neutral L ligands. The six-coordination of every Co(II) atom (Fig. 3) may be described as a very flattened tetrahedron (atoms N(101), N(103), N(201), N(203) for Co(1) and N(301), N(303), N(401), N(403) for Co(2))

TABLE 4. Planar moieties in cations **Ia** and **Ib** (atoms Co(1) and Co(2) were not included in the calculation of mean planes)[a]

Plane A	$6.009x+2.319y+18.269z=2.4862$								
N(101)	C(114)	N(105)	C(120)	C(115)	C(119)	C(118)	C(117)	C(116)	Co(1)
0.0025	0.0044	0.0032	0.0082	0.0044	−0.0392	0.0369	−0.0003	−0.0200	−0.0136
Plane B	$6.664x-0.887y+18.041z=0.7888$								
N(103)	C(108)	N(104)	C(105)	C(106)	C(104)	C(103)	C(102)	C(101)	Co(1)
0.0271	0.0017	−0.0223	0.0001	0.0061	−0.0092	0.0383	−0.0161	−0.0257	0.3067
Plane C	$4.450x+1.827y+19.016z=2.5206$								
N(102)	C(109)	C(110)	C(111)	C(112)	C(113)				Co(1)
−0.0012	−0.0138	0.0252	−0.0215	0.0064	0.0050				−0.3002
Plane D	$2.756x+17.603y-5.282z=7.3583$								
N(201)	C(214)	N(205)	C(220)	C(215)	C(219)	C(218)	C(217)	C(216)	Co(1)
0.0350	0.0065	0.0017	−0.0359	−0.0208	0.0156	−0.0054	0.0453	−0.0420	0.1612
Plane E	$2.913x+18.175y-1.634z=7.7239$								
N(203)	C(208)	N(204)	C(205)	C(206)	C(204)	C(203)	C(202)	C(201)	Co(1)
−0.0045	0.0155	−0.0209	0.0148	−0.0099	0.0117	−0.0133	0.0055	0.0012	0.2778
Plane F	$4.001x+17.543y-4.0757z=7.8156$								
N(202)	C(209)	C(210)	C(211)	C(212)	C(213)				Co(1)
0.0119	0.0016	−0.0197	0.0239	−0.0109	−0.0068				−0.1780
Plane G	$11.966x+1.404y+12.741z=11.1510$								
N(301)	C(314)	N(305)	C(320)	C(315)	C(319)	C(318)	C(317)	C(316)	Co(2)
−0.0811	0.0919	−0.0036	−0.0237	0.0737	−0.0670	−0.0644	−0.0105	0.0848	0.0823
Plane H	$11.771x+2.081y+12.930z=11.4174$								
N(303)	C(308)	N(304)	C(305)	C(306)	C(304)	C(303)	C(302)	C(301)	Co(2)
0.0381	−0.0306	−0.0192	0.0138	0.0396	0.0374	0.0415	−0.0133	−0.0282	0.0407
Plane I	$13.147x+1.456y+10.662z=11.0153$								
N(302)	C(309)	C(310)	C(311)	C(312)	C(313)				Co(2)
−0.0038	0.0025	0.0125	−0.0249	0.0236	−0.0099				−0.2174
Plane J	$2.303x+16.807y-7.965z=2.6629$								
N(401)	C(414)	N(405)	C(420)	C(415)	C(419)	C(418)	C(417)	C(416)	Co(2)
−0.0061	−0.0286	0.0135	0.0101	0.0115	0.0138	−0.0249	−0.0354	0.0460	0.1496
Plane K	$1.770x+17.810y-5.167z=4.0986$								
N(403)	C(408)	N(404)	C(405)	C(406)	C(404)	C(403)	C(402)	C(401)	Co(2)
−0.0964	0.1031	−0.0067	0.0010	0.0871	−0.0871	−0.0935	−0.0018	0.0962	0.0896
Plane L	$2.554x+17.243y-6.649z=3.4738$								
N(402)	C(409)	C(410)	C(411)	C(412)	C(413)				Co(2)
0.0102	−0.0077	0.0008	0.0041	−0.0017	−0.0057				0.1833

[a] The dihedral angles between the mean planes are: A/B 10.2°, A/C 6.0°, B/C 11.8°, D/E 10.6°, D/F 5.7°, E/F 8.3°, G/H 2.3°, G/I 7.4°, H/I 8.5°, J/K 8.8°, J/I 4.1° and K/L 5.4°.

with two additional pseudo-axial substituents (atoms N(102), N(202) for Co(1) and N(302), N(402) for Co(2)).

A similar coordination, described as a highly distorted [Co(II)–N_6] octahedron was found for Co(II) atom in the crystal structure of [Co(terpy)$_2$]I_2(H_2O)$_2$ (**II**) [10]. This structure was determined at the temperatures of 295 and 120 K (magnetic measurements indicate a gradual decrease of the magnetic moment from 3.66 BM at 295 K to 2.20 BM at 120 K). The structure at 120 K may be considered as corresponding to a pure low-spin state (^2E), at 295 K to about halfway between low-spin and high-spin ($^4T_1$) states. In **II**, at 295 K the Co–N bond length to the central pyridine ring of 1.942 Å is shorter than to that to the peripheral pyridine ring (2.104 Å). The Co–N bond to the central ring decreases by 0.030 Å, and the peripheral by 0.021 Å on transition from 295 to 120 K [6]. As was noted in ref. 6, the ground states ^2E and $^4T_1$ in complexes [Co(terpy)$_2$]X_2 can be directly mixed by spin–orbit coupling assuming adiabatic character for the spin-state transition.

In the crystal of the only structurally studied metal complex of bis(1′-methylbenzimidazol-2′-yl)pyridine CuL_2(ClO_4)$_2$(H_2O) (**III**) only one L ligand (A) coordinates the Cu atom in a tridentate manner with Cu–N(pyridine) distances shorter than the two Cu–N(benzimidazol) distances (1.973(5) versus 2.004(5) and 2.042(5) Å, respectively) [4]. The second ligand (B) forms one normal coordination bond at 1.958(5) Å and one very long bond of 2.510(5) Å*. A similar

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*The bond order for this interaction is according to Pauling [11] about $n=1/6$.

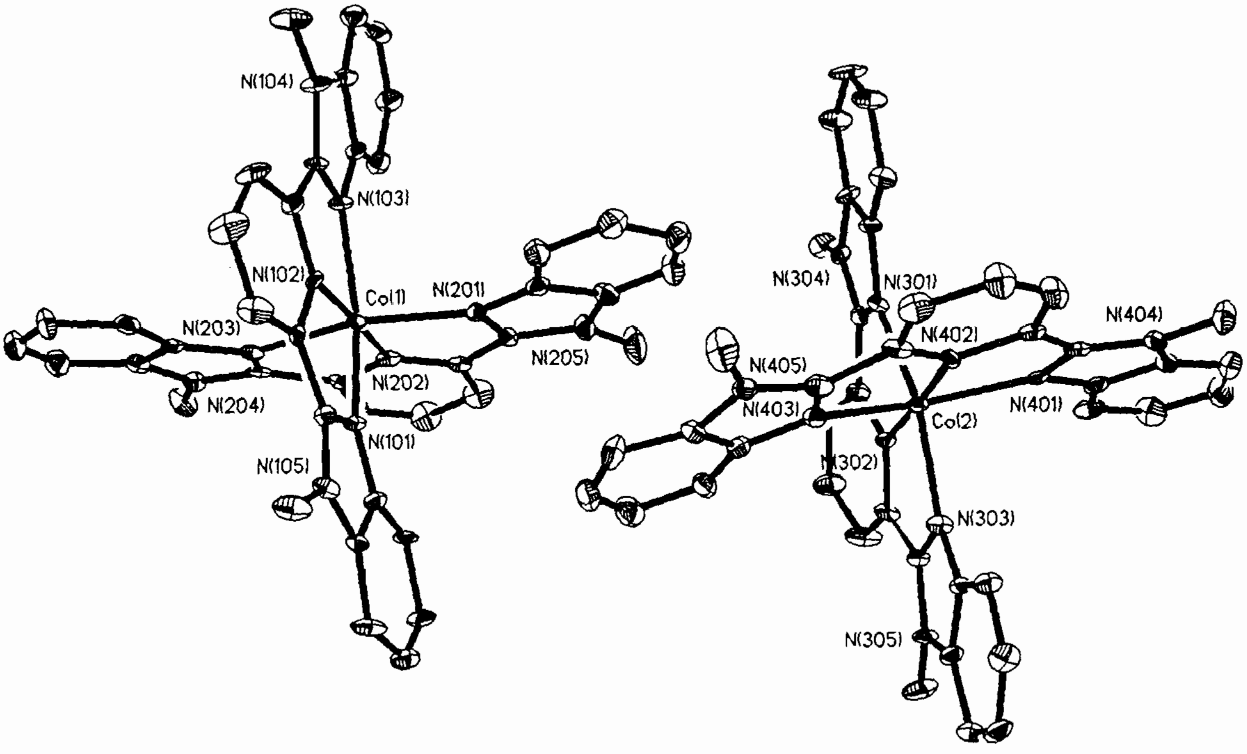

Fig. 1. Structure of symmetrically independent cations **Ia** and **Ib**.

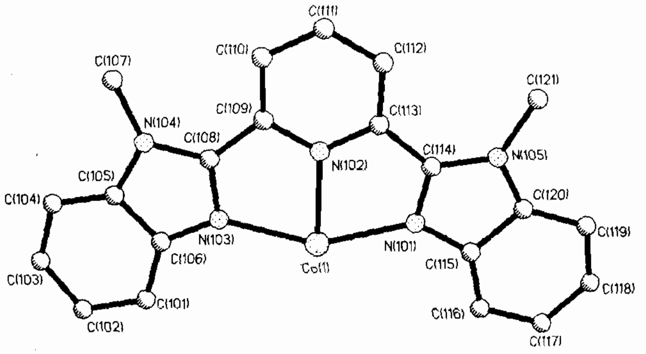

Fig. 2. Ligand L of the cation **Ia** with atom numbering. The atoms in the second L ligand of **Ia** and in the two L ligands of **Ib** are numbered in a similar way (atoms N(201), N(202), N(203), N(204) of **Ia**, N(301), N(302), N(303), N(304) and N(401), N(402), N(403), N(404) of **Ib** correspond to N(201), N(102), N(203), N(204), of **Ia**, see Fig. 1).

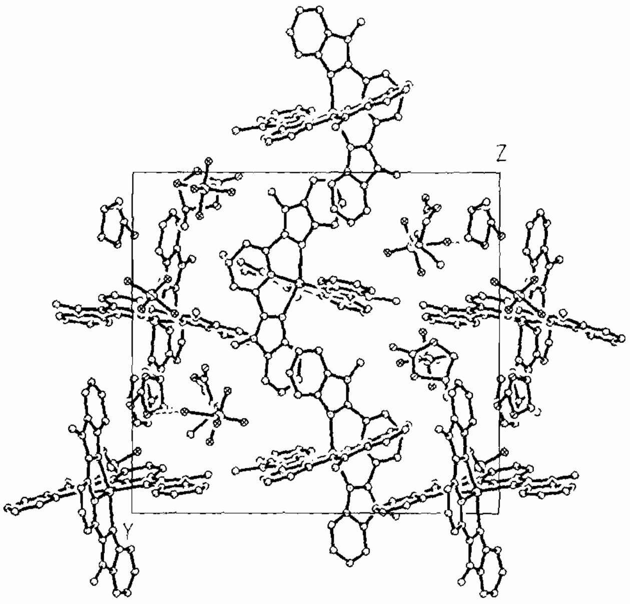

Fig. 3. Projection of crystal structure **I** along [100].

coordination is shown by the Fe(II) atoms in the crystal $[Fe(bzimpy)_2](CF_3SO_3)_2 2EtOH$ (**IV**) [7].

In the closely related complex $[CuL'(CH_3CN)(ClO_4)](ClO_4)$ (L' = bis(benzimidazol-2'-yl)pyridine) the central Cu–N distance to the pyridine group is also shorter than the two bonds to the imidazol groups (1.966(2), 2.023(2) and 2.028(2) Å, respectively) [4].

Like in complexes **II** and **III**, the central Co–N(pyridine) bond lengths in the cations **Ia** and **Ib** are shorter than the Co–N(benzimidazol) bonds (av. values are 2.074 and 2.120 Å for **Ia** and 2.079 and 2.122 Å for **Ib**). The angles NCoN between the neighbouring pseudo-equatorial Co–N bonds are 91.7–94.4° for the Co(1) atom and 91.2–95.3° for the Co(2) atom. The bond angle between the pseudo-axial N atoms which belong to pyridine moieties is close to 180°

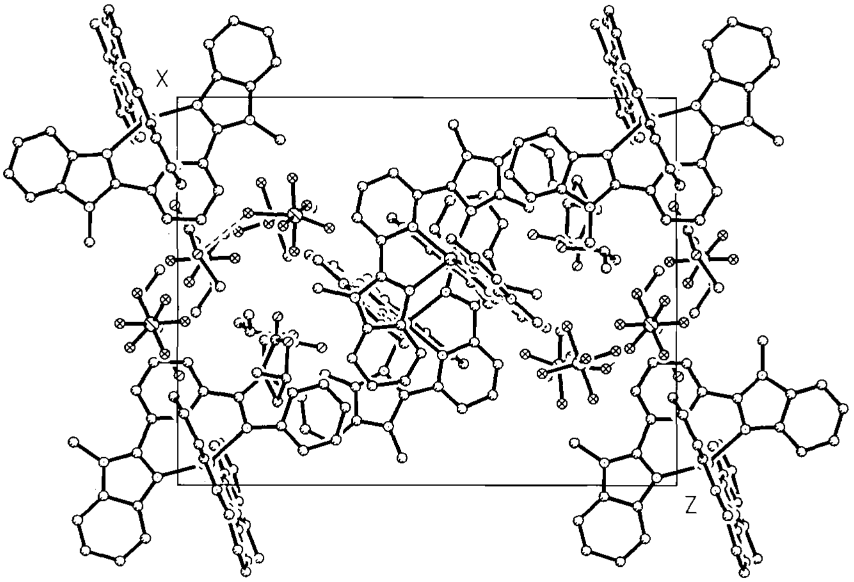

Fig. 4. Projection of crystal structure **I** along [010].

(176.2° for N(102)Co(1)N(202) and 176.8° for N(302)Co(2)N(402)). In **II** the N–Co–N angle between the Co–N bonds to the central N atoms equals 180.0° at both 295 and 120 K temperatures (the cation $[Co(terpy)_2]^{2+}$ retains S_4 symmetry). The bond angles between the distal N atoms of the chelate L ligands are 152.5, 152.6° for **Ia** and 151.3, 151.9° for **Ib**. In **II** the bond angle N(distal)–Co–N(distal) increases from 157.0° (295 K) to 158.9° (120 K). In **III** the corresponding N–Co–N bond angle equals 159.1(2)°.

The ligand A in **III** is not planar, the benzimidazole rings form angles of 7.6(2) and 14.8(2)° with the pyridine ring. All four symmetrically independent ligands L in the crystal structure **I** are only approximately flat, the dihedral angles between the pyridine rings and neighbouring benzimidazol moieties vary from 4.1 to 11.8° (Table 4).

The cations **Ia** and **Ib** are arranged in the crystal structure **I** into separate chains with Co...Co distances of 9.760 and 9.809 Å around the screw axes 2_1 $(0, y, 0)$ and 2_1 $(\frac{1}{2}, y, \frac{1}{2})$, respectively (see Fig. 3). By their development, the alternating chains of cations **Ia** and **Ib** form sheets parallel to the plane (101) of crystal **I** with intersheet separation of $d_1 = 12.31$ Å (Fig. 4). From the point of view of crystal packing, two types of ligand L at every Co atom may be distinguished. Through the van der Waals contacts ...**Ia**...**Ia**... and ...**Ib**...**Ib**... of the ligands of the first type the cations are arranged in the above mentioned chains. Through the contacts ...**Ia**...**Ib**...**Ia**... of the ligands of the second type the cations **Ia** and **Ib** are arranged into the sheets. There are no direct intercationic contacts between the different sheets. The anions PF_6^- and the solvent molecules 4-methyl-1,3-dioxolan-2-on are located between these sheets. There are no intermolecular contacts in structure **I** which are shorter than the sums S of van der Waals radii of corresponding atoms [12]. The majority of the shortest contacts (<3.50 Å) are formed by the O atoms of the solvent molecules and F atoms of PF_6^- anions: O...O 3.400, 3.435 Å ($S = 3.00$ Å), O...N 3.320, 3.254 Å (3.20 Å), O...F 3.173–3.472 Å (six contacts, $S = 2.97$ Å), F...F 3.186 Å ($S = 2.94$ Å). The Co sheets parallel to the *ac* plane may be also distinguished with the shortest Co(1)...Co(2) distance of 9.875 Å and intersheet separation of $d_2 = b/2 = 9.281$ Å.

The crystallographic aspect of the processes of liberation of low-molecular-weight products as a result of chemical reactions in organic crystals as well as desolvation of crystalline solvates are discussed in ref. 13. The high crystallinity of the pattern (c) and close similarity of all patterns (a)–(c) on Fig. 5 clearly indicate the conservation of the main features of structure **I** after desolvation, i.e. the topotacticity of the desolvation of crystal **I**. One may suggest that the chains of cations are conserved in the product of desolvation because they do not contain solvent molecules. Moreover, the desolvation does not essentially change the distances between the chains of cations (the position of the majority of peaks on the patterns (a)–(c) are retained), and leads to redistribution of positions of solvent molecules into the sheets. The easiness of solvent loss was also noticed for crystal **IV**, which has the sheet cation structure as well [7].

Conclusions

The X-ray single crystal diffraction study at 250 K indicates the composition $(CoL_2)(PF_6)_2(C_4H_6O_3)_3$ of

TABLE 5. Powder diffraction patterns of **I** sealed in the capillary with mother liquid (a), left in air for one day (b) and left in air for one week (c)

(a)		(b)		(c)		*hkl*[a]
2θ	I	2θ	I	2θ	I	
6.45	30	6.46	31	6.42	29	011
				6.84	18	
7.11	100	7.10	100	7.08	100	−101
7.33	23	7.33	25	7.30	25	110
8.55	17	8.58	38	8.55	43	111
8.75	10			8.74	11	002
				8.95	12	
		9.17	35	9.15	46	
9.49	32	9.50	34	9.47	32	020
		9.89	14	9.84	19	
11.03	11	11.02	12	10.99	15	120
		11.27	35	11.24	43	200
11.43	9			11.44	12	−112, 112
		11.72	18	11.69	27	
12.18	12	12.18	12	12.16	15	210
12.94	40	12.94	36	12.91	39	022, −211
		14.10	51	14.06	60	−122, 122
14.25	53					−202
		14.57	64	14.55	81	
14.92	32	14.93	37	14.90	43	031
		15.24	16	15.21	21	
15.96	9	15.96	12	15.95	14	131, −131
16.24	16	16.26	14	16.23	14	023
		17.21	19	17.23	19	−123, 123
17.34	15					−203, 203
17.69	88	17.68	91			−132, 132
				17.83	92	
18.06	61	18.05	53	18.03	49	−311, 311
18.46	17	18.44	38	18.41	40	−104, 104
18.70	34	18.71	37	18.68	33	−231, 231
19.06	36	19.06	36	19.03		−302, 040, 302, −114, 114
19.38	13	19.37	161	9.33	11	320
19.59	41	19.59	52	19.56	47	041
19.88	49	19.86	55			140, −321
				20.00	55	024
20.22	9	20.23	18	20.21	15	−232, 232, −133
		20.59	63	20.55	70	
20.90	31					−204, 204
		21.01	69	20.99	76	042
21.45	46	21.44	44	21.42	38	−214, −303, 214, 303
21.76	42	21.76	39	21.73	35	−142, 142
21.98	16	21.99	26	21.95	22	−313
22.59	32	22.58	36	22.55	32	015, −331, −241, 331, 241
23.01	12	23.02	20	22.98	20	−401, 401, −224, 224
23.23	14	23.22	20			043, −115, 115
23.47	16	23.42	27	23.39	30	−411, 411
				23.59	11	
23.87	22	23.86	24	23.84	23	−332, −242, 050, 332, 242
		24.29	17	24.26	16	402, −402
24.47	16					−304, 304
		24.75	19	24.75	18	412
24.92	16					−314, −421, 421, −151, 151, 314
		25.09	11	25.08	14	
		25.33	15	25.30	22	
25.85	11	25.84	11	25.83	13	−333, −243, 333, 243
26.11	21	26.12	22	26.09	21	422, −152, 152
26.63	13	26.61	11	26.59	14	−225, 225, −413

(*continued*)

TABLE 5. (*continued*)

(a)		(b)		(c)		*hkl*[a]
2*θ*	*I*	2*θ*	*I*	2*θ*	*I*	
27.92	17	27.93	13	27.92	16	305, −252, 252, −423, −153, 423, 153
28.27	12	28.36	21	28.32	27	432, −315, 500
28.73	18	28.64	45	28.61	56	−235, 510, 235, −404
		28.84	13	28.84	16	126, −343, 343, −206
29.09	14	29.09	15	29.05	16	511, 061
29.30	14	29.31	13	29.29	17	−216, 045, 216, 160
29.67	14	29.67	13	29.65	14	−161, 161, −253, 253, −502, 440, 502

[a] Indexed in the unit cell of **I** at 250 K, see Table 1.

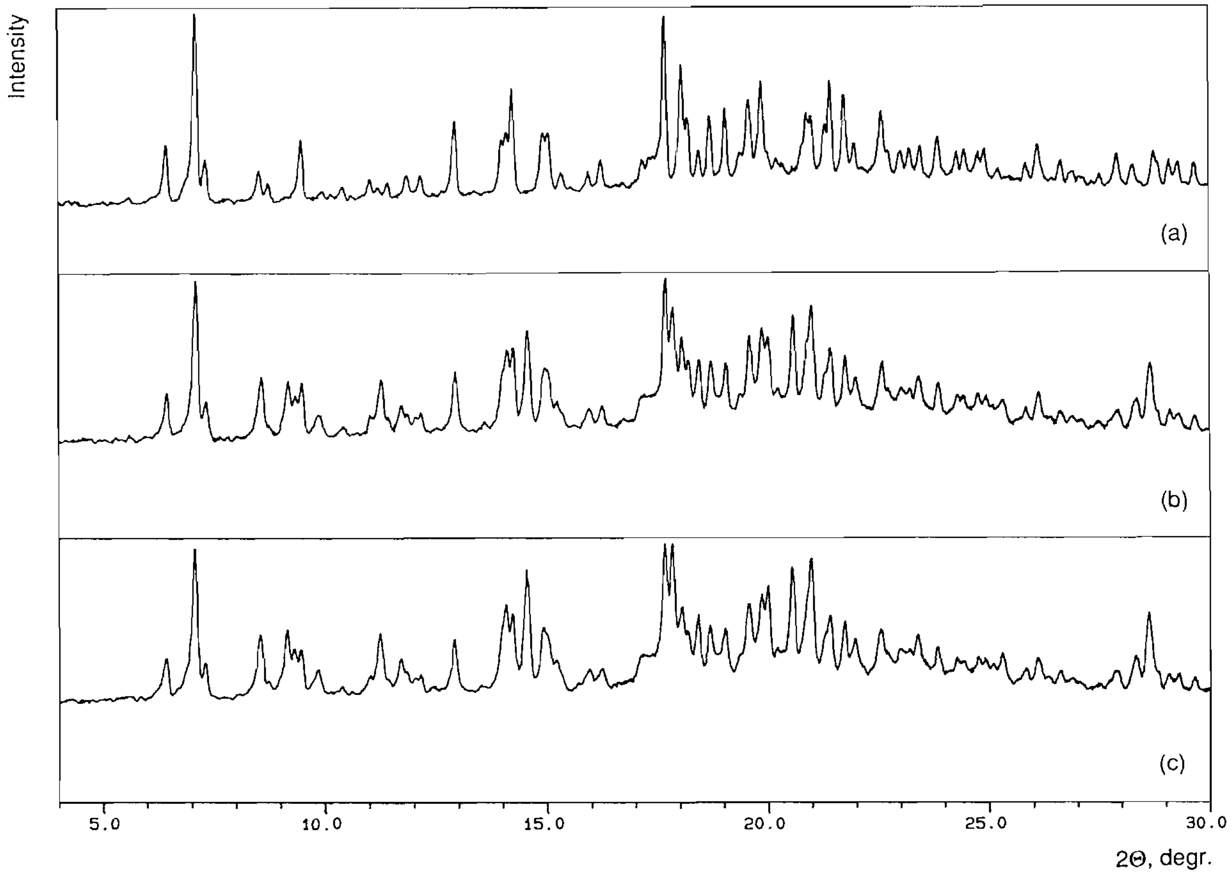

Fig. 5. Powder diffraction patterns of *I* quickly sealed in the capillary with mother liquid (a), exposed to air for one day (b) and for one week (c).

crystal **I** obtained by crystallization of $(CoL_2)_2 \cdot (PF_6)_2$ from the acetonitrile/4-methyl-1,3-dioxolan-2-on mixture. This allows structure **I** to be considered as a solid state precursor of the corresponding electrolyte system with the $(CoL_2)^{2+}/(CoL_2)^{3+}$ redox pair. The hexacoordination of Co atoms in the cations $(CoL_2)_2{}^{2+}$ with slightly shortened pseudo-axial Co–N(pyridine) distances in comparison with the Co–N(imidazol) distances agrees with literature data on related Co complexes. The analysis of crystal packing indicates a tendency of $(CoL_2)^{2+}$ to associate into infinite motifs (chains, sheets) with the anions and solvent molecules between them.

Supplementary material

Details of data collection, structure solution, H atom coordinates, displacement parameters and a listing of observed and calculated structure factors can be obtained from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2. Request should be accompanied by the complete literature citation.

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