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Crystal structure of *catena*-poly[dichlorido-(μ_2 -1,5-dimethyl-2-phenyl-4-((pyridin-4-ylmethylene)amino)-1,2-dihydro-3*H*-pyrazol-3-one- κ^2 N:O)cobalt(II)] – methanol (1/1), C₁₈H₂₀Cl₂CoN₄O₂

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.10 × 0.06 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.09 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	27.9°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	18542, 5019, 0.093
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2399
$N(\text{param})_{\text{refined}}$:	253
Programs:	Bruker programs [1], SHELX [2, 3]

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Abstract

C₁₈H₂₀Cl₂CoN₄O₂, monoclinic, $P2_1/n$ (no. 14), $a = 9.4744(18)$ Å, $b = 18.084(3)$ Å, $c = 12.290(2)$ Å, $\beta = 94.196(3)^\circ$, $V = 2100.1(7)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0559$, $wR_{\text{ref}}(F^2) = 0.1705$, $T = 296(2)$ K.

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

Source of materials

The title compound was synthesized by mixing 0.146 g (0.5 mmol) 1,5-dimethyl-2-phenyl-4-((pyridin-4-ylmethylene)amino)-1*H*-pyrazol-3(2*H*)-one, (L4) which was prepared according to the literature [4]), 0.199 g (0.83 mmol) CoCl₂ · H₂O, 9 mL absolute methanol and 0.5 mL dichloromethane in a 25 mL polytetrafluoroethylene reactor. Then the polytetrafluoroethylene reactor was placed in an oven at 90 °C. After 7 days, dark green granular crystal was

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

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.26123(16)	0.21811(11)	0.53018(11)	0.0994(6)
Cl2	0.08905(13)	0.11800(7)	0.28153(12)	0.0747(4)
N1	0.3118(4)	−0.19910(18)	0.2163(3)	0.0490(9)
N2	0.5605(4)	0.02693(18)	0.3679(3)	0.0485(9)
N3	0.7590(3)	0.1822(2)	0.4636(3)	0.0517(9)
N4	0.6432(3)	0.21862(18)	0.4131(3)	0.0486(9)
O1	0.4388(3)	0.18744(15)	0.3108(2)	0.0519(8)
O2 ^a	0.679(3)	0.1050(11)	0.0933(16)	0.359(11)
H2A ^a	0.6842	0.1494	0.1065	0.538*
O2 ^b	0.814(13)	0.154(6)	0.163(10)	0.359(11)
H2 ^b	0.8999	0.1515	0.1784	0.538*
Co1	0.24525(6)	0.20112(3)	0.35000(5)	0.0502(2)
C1	0.2319(5)	−0.1399(3)	0.1901(4)	0.0663(14)
H1	0.1469	−0.1464	0.1484	0.080*
C2	0.2706(5)	−0.0703(3)	0.2224(4)	0.0681(14)
H2	0.2113	−0.0307	0.2032	0.082*
C3	0.3973(5)	−0.0577(2)	0.2835(4)	0.0500(11)
C4	0.4764(4)	−0.1196(2)	0.3127(4)	0.0515(11)
H4	0.5599	−0.1145	0.3568	0.062*
C5	0.4335(5)	−0.1879(2)	0.2775(4)	0.0529(11)
H5	0.4905	−0.2284	0.2966	0.063*
C6	0.4433(5)	0.0166(2)	0.3147(4)	0.0536(11)
H6	0.3857	0.0568	0.2952	0.064*
C7	0.6091(4)	0.0975(2)	0.3945(3)	0.0442(10)
C8	0.7370(4)	0.1094(2)	0.4516(4)	0.0483(10)
C9	0.5498(4)	0.1678(2)	0.3672(4)	0.0473(10)
C10	0.8421(5)	0.0535(3)	0.4948(4)	0.0654(13)
H10A	0.9292	0.0601	0.4607	0.098*
H10B	0.8060	0.0047	0.4791	0.098*

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H10C	0.8588	0.0595	0.5722	0.098*
C11	0.8778(5)	0.2222(3)	0.5135(5)	0.0768(16)
H11A	0.8475	0.2516	0.5725	0.115*
H11B	0.9162	0.2538	0.4603	0.115*
H11C	0.9491	0.1879	0.5410	0.115*
C12	0.6394(4)	0.2969(2)	0.3981(4)	0.0490(10)
C13	0.6162(5)	0.3428(3)	0.4830(4)	0.0661(14)
H13	0.6028	0.3238	0.5518	0.079*
C14	0.6130(7)	0.4179(3)	0.4648(6)	0.092(2)
H14	0.5973	0.4498	0.5220	0.110*
C15	0.6324(7)	0.4463(3)	0.3642(8)	0.102(2)
H15	0.6304	0.4971	0.3530	0.122*
C16	0.6548(7)	0.3998(4)	0.2810(6)	0.097(2)
H16	0.6669	0.4190	0.2121	0.116*
C17	0.6596(5)	0.3254(3)	0.2968(5)	0.0712(15)
H17	0.6765	0.2940	0.2393	0.085*
C18 ^a	0.542(2)	0.0874(10)	0.0512(15)	0.251(8)
H18A ^a	0.4662	0.1026	0.0939	0.377*
H18B ^a	0.5380	0.0349	0.0405	0.377*
H18C ^a	0.5331	0.1119	−0.0183	0.377*
C18 ^b	0.778(18)	0.115(8)	0.065(10)	0.251(8)
H18D ^b	0.8109	0.1263	−0.0050	0.377*
H18E ^b	0.6788	0.1255	0.0647	0.377*
H18F ^b	0.7939	0.0634	0.0808	0.377*

Occupancies: ^a = 877(14), ^b = 0.123(14).

separated out with 82% yield. Elemental Analysis (%; measured/theoretical): C, 47.59/47.56; H, 4.43/4.41; Co, 12.97/13.00; N, 12.33/12.37; O, 7.04/7.01. IR (cm^{−1}, KBr pellet): 3400(w), 1618(m), 1595(m), 1539(s), 1490(m), 1427(m), 1026(m), 833(w).

Comment

In recent years, studies on the Schiff complexes which were prepared by Co(II) and antipyrine [5–7] have attracted extensive attention. On the one hand, Schiff base has good chemical coordination properties, unique electrical and optical properties, and special biological activity [8, 9]. On the other hand, Schiff bases have excellent oxygen carrying capacity after forming complexes with metals. Thus they are important in the fields of coordination biochemistry, organic catalysis, analytical chemistry, and functional materials.

Herein, the complex of Co(II) and ligand L4 is synthesized. The smallest asymmetric unit of the complex consists of one Co(II), one ligand L4 carbonyl two chlorido ligands, and one methanol molecule which is disordered. The molecular metal center Co(II) adopts the four-coordinated form of {ONCl₂} to build a slightly distorted tetrahedron. The coordinating atoms are derived from the carbonyl oxygen atom in ligand L4 of one molecule, the nitrogen atom on the pyridine

ring of another adjacent ligand L4, and two chlorido ligands. The Co–Cl bond lengths are 2.2298(16) and 2.2306(14) Å; the bond angle Cl1–Co1–Cl2 is 117.53(7)°. The bond length N1–Co1 is 2.037(3) Å; similar to that reported in the literature [10]; the bond length of Co1–O1 is 1.946(3) Å, which is similar to that reported [11].

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References

1. Bruker. SMART and SAINT. Bruker AXS Inc., Madison, WI, USA (2007).
2. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal refinement with SHELX. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Montalvo-Gonzalez, R.; Ariza-Castolo, A.: Experimental and DFT studies on the vibrational and electronic spectra of 1, 5-dimethyl-2-phenyl-4-[(pyridin-4-ylmethylene)-amino]-1, 2-dihydro-pyrazol-3-one. *Spectrochim. Acta A* **77** (2010) 732–739.
5. Xu, C.; Zheng, H.; Hu, B.; Liu, X.; Lin, L.; Feng, X.: Chiral cobalt(II) complex catalyzed Friedel-Crafts aromatization for the synthesis of axially chiral biaryldiols. *Chem. Commun.* **53** (2017) 9741–9744.
6. Wang, W.; Li, J.; Yin, L.; Zhao, Y.; Ouyang, Z.; Wang, X.; Wang, Z.; Song, Y.; Power, P. P.: Half-sandwich metal carbonyl complexes as precursors to functional materials: from a near-infrared-absorbing dye to a single-molecule magnet. *J. Am. Chem. Soc.* **139** (2017) 12069–12075.
7. Zorina-Tikhonova, E. N.; Gogoleva, N. V.; Sidorov, A. A.: 36-Nuclear anionic dimethylmalonate complexes of nickel(II) and cobalt(II) with cation of NBu₄⁺: synthesis, structure and magnetic properties. *Polyhedron* **130** (2017) 67–74.
8. Cui, H. H.; Wang, J.; Chen, X. T.; Xue, Z. L.: Slow magnetic relaxation in five-coordinate spin-crossover cobalt(II) complexes. *Chem. Commun.* **53** (2017) 9304–9307.
9. Yuan, G.; Tian, Y.; Liu, J.: Schiff base anchored on metal-organic framework for Co(II) removal from aqueous solution. *Chem. Eng. J.* **326** (2017) 691–699.
10. Chavez, F. A.; Nguyen, C. V.; Olmstead, M. M.; Mascharak, P. K.: Synthesis, properties, and structures of a stable cobalt(III) alkyl peroxide complex and its role in the oxidation of cyclohexane. *Inorg. Chem.* **35** (1996) 6282–6291.
11. Wang, W.; Yuan, W.-J.; Liu, Q.-L.; Lei, Y.-N.; Qi, S.; Gao, Y.: Selective fluorescence sensor for Cu²⁺ with a novel triazole Schiff-base derivative with coumarin units. *Het. Commun.* **20** (2014) 241–247.