# Crystal structure of bis(4-benzoyl-3-methyl-1-phenyl pyrazol-5-one)-bis(*N*,*N*-dimethylformamide)cobalt(II), $C_{40}H_{40}CoN_6O_6$

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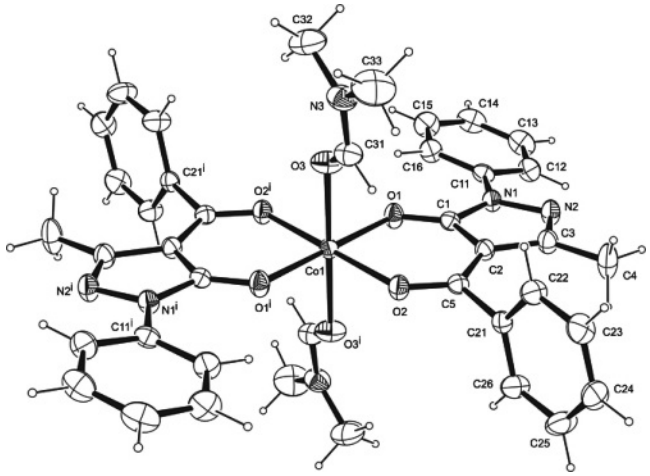


**Abstract**

$C_{40}H_{40}CoN_6O_6$, monoclinic, $P2_1/n$ (no. 14), $a$ = 10.1110(5) Å, $b$ = 9.3804(4) Å, $c$ = 18.9754(8) Å, $\beta$ = 91.037(2)°, $V$ = 1799.4 Å$^3$, $Z$ = 2, $R_{gt}(F)$ = 0.0270, $wR_{ref}(F^2)$ = 0.0743, $T$ = 200 K.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | orange blocks, size 0.223×0.437×0.559 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 5.34 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX-II CCD, $\varphi$ and $\omega$ |
| $2\theta_{max}$: | 56.73° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 49492, 4515 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 4132 |
| $N(param)_{refined}$: | 244 |
| Programs: | SHELX, SADABS, SAINT, ShelXLe, ORTEP-3, PLATON, MERCURY [9–14] |

## Source of material

To a solution of *Bmpp*-Sn (4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide, 2 mmol, 0.87 g) in hot ethanol (40 mL) was added in drops aqueous solution of $CoCl_2{\cdot}4H_2O$ (1 mmol, 0.20 g) while stirring under reflux. After 4 h of reflux, the pink precipitate was filtered, washed with ethanol/water (1:1), dried at room temperature and stored over fused $CaCl_2$. Slow evaporation of a solution of the resultant pink solid in dimethylformamide DMF afforded orange crystals of the titled metal complex of the Schiff base precursor $Co(Bmpp)_2(DMF)_2$ suitable for X-ray crystallography.

## Experimental details

Carbon-bound H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with $U_{iso}$(H) set to 1.2 $U_{eq}$(C). The H atoms of the methyl groups were allowed to rotate with a fixed angle around the C–C bond to best fit the experimental electron density (HFIX 137 in the SHELX program suite [9]), with $U_{iso}$(H) set to 1.5 $U_{eq}$(C).

## Discussion

Acylpyrazolones have shown to be good heterogeneous catalysts [1]. Because of their chelating property, they have been used as analytical reagents for the determination of trace amount of metals in solutions [2]. Their structure and reactivity enable them to form an important class of compounds with amines known as Schiff bases [3, 4], which have been revealed to have superior bioactive properties [5]. On successful coordination of acylpyrazolone with transition metal ions their catalytic properties amongst others may increase [6]. We already have reported a bioactive cobalt complex of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one with two ethanol ligands in *trans* position [7]. In continuation of our study on acylpyrazolone and its transition metal complexes, presented herein is the molecular and crystal structure of a similar cobalt complex of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one with DMF obtained from the reaction of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one sulfanilamide *Bmpp*-Sn with a cobalt salt. The crystal structure of the title complex has an octahedral geometry with two *trans Bmpp* ligands and two coordinating dimethylformamide molecules. The complex is centrosymmetrical with the Co atom occurring on an inversion center and half the complex in the asymmetric unit. Each *Bmpp* ligand is deprotonated with the negative charge to be delocalized. The Co–O bond lengths to the *Bmmp* ligand O1 and O2 are 2.0384(8) and 2.0921(8) Å, respectively. The Co–O bond to DMF is slightly longer at 2.1188(10) Å. A search in the Cambridge Structural Database [8] for deposited structures with similar Co, $O_2$, $C_3$ six membered rings shows that the median Co–O bond length is 2.041 Å. The phenyl rings C11–C16 and C21–C26 of the *Bmmp* ligand are turned out of the main Co1, O1 and O2 least square plane by 11.84(5) and 88.23(5)° respectively. There are two potential intramolecular hydrogen bonds within the *Bmmp* ligand C12–H12···N2 and C16–H16···O1 with bond lengths of 2.43 and 2.28 Å respectively. The DMF has one intramolecular C32–H32C···O3 hydrogen bond of length 2.37 Å and one intramolecular hydrogen bond to *Bmmp* C31–H31···O2 of length 2.49 Å. There are no notable intermolecular hydrogen bonds, but there are C23–H23···$\pi$ ring interactions with the C11–C16 phenyl rings that links an infinite chain of complexes in the *a*-axis direction. The H23 to centroid distance is 2.63 Å and the dihedral angle between the two phenyl least square planes is 81.23(6)°.

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**Table 2.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(4A) | 4*e* | –0.1135 | 0.7630 | 0.0504 | 0.062 |
| H(4B) | 4*e* | –0.0039 | 0.7676 | 0.1123 | 0.062 |
| H(4C) | 4*e* | –0.0686 | 0.6188 | 0.0890 | 0.062 |
| H(12) | 4*e* | 0.0021 | 0.8795 | –0.1500 | 0.034 |
| H(13) | 4*e* | 0.0002 | 0.9417 | –0.2692 | 0.042 |
| H(14) | 4*e* | 0.1592 | 0.8510 | –0.3445 | 0.043 |
| H(15) | 4*e* | 0.3215 | 0.6979 | –0.2998 | 0.042 |
| H(16) | 4*e* | 0.3246 | 0.6314 | –0.1811 | 0.034 |
| H(22) | 4*e* | 0.0929 | 0.4070 | 0.1519 | 0.033 |
| H(23) | 4*e* | –0.0146 | 0.4353 | 0.2591 | 0.040 |
| H(24) | 4*e* | 0.0238 | 0.6380 | 0.3271 | 0.041 |
| H(25) | 4*e* | 0.1755 | 0.8087 | 0.2909 | 0.044 |
| H(26) | 4*e* | 0.2883 | 0.7776 | 0.1854 | 0.036 |
| H(31) | 4*e* | 0.3365 | 0.2642 | 0.0615 | 0.035 |
| H(32A) | 4*e* | 0.2664 | 0.0129 | –0.0898 | 0.072 |
| H(32B) | 4*e* | 0.3845 | –0.0737 | –0.0523 | 0.072 |
| H(32C) | 4*e* | 0.4126 | 0.0784 | –0.0873 | 0.072 |
| H(33A) | 4*e* | 0.1535 | –0.0081 | 0.0341 | 0.085 |
| H(33B) | 4*e* | 0.2302 | 0.0698 | 0.0977 | 0.085 |
| H(33C) | 4*e* | 0.2852 | –0.0774 | 0.0672 | 0.085 |

**Table 3.** Atomic coordinates and displacement parameters (in Å$^2$).

| Atom | Site | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Co(1) | 2*d* | ½ | ½ | 0 | 0.0167(1) | 0.0220(1) | 0.0169(1) | 0.00120(7) | 0.00028(7) | 0.00015(7) |
| O(1) | 4*e* | 0.36339(8) | 0.59842(9) | –0.06357(4) | 0.0208(4) | 0.0364(4) | 0.0192(4) | 0.0066(3) | 0.0020(3) | 0.0031(3) |
| O(2) | 4*e* | 0.37678(8) | 0.52131(9) | 0.08676(4) | 0.0211(4) | 0.0323(4) | 0.0197(4) | 0.0052(3) | 0.0012(3) | 0.0016(3) |
| O(3) | 4*e* | 0.4205(1) | 0.2964(1) | –0.02413(5) | 0.0441(5) | 0.0293(4) | 0.0276(4) | –0.0105(4) | –0.0017(4) | –0.0014(3) |
| N(1) | 4*e* | 0.15771(9) | 0.7044(1) | –0.08279(5) | 0.0193(4) | 0.0280(5) | 0.0175(4) | 0.0025(3) | 0.0007(3) | 0.0022(3) |
| N(2) | 4*e* | 0.04436(9) | 0.7371(1) | –0.04498(5) | 0.0207(4) | 0.0380(5) | 0.0218(4) | 0.0067(4) | 0.0021(3) | 0.0026(4) |
| N(3) | 4*e* | 0.3197(1) | 0.0906(1) | 0.00477(6) | 0.0351(5) | 0.0248(5) | 0.0381(6) | –0.0046(4) | –0.0057(4) | 0.0019(4) |
| C(1) | 4*e* | 0.2521(1) | 0.6372(1) | –0.04155(5) | 0.0194(5) | 0.0204(5) | 0.0179(5) | –0.0009(4) | –0.0011(4) | 0.0003(4) |
| C(2) | 4*e* | 0.1957(1) | 0.6283(1) | 0.02701(5) | 0.0185(5) | 0.0243(5) | 0.0178(5) | 0.0006(4) | 0.0015(4) | 0.0006(4) |
| C(3) | 4*e* | 0.0673(1) | 0.6921(1) | 0.01946(6) | 0.0216(5) | 0.0336(6) | 0.0206(5) | 0.0040(4) | 0.0010(4) | 0.0016(4) |
| C(4) | 4*e* | –0.0388(1) | 0.7121(2) | 0.07231(7) | 0.0263(6) | 0.072(1) | 0.0259(6) | 0.0186(6) | 0.0058(5) | 0.0086(6) |
| C(5) | 4*e* | 0.2636(1) | 0.5765(1) | 0.08752(5) | 0.0200(5) | 0.0182(5) | 0.0186(5) | –0.0026(4) | 0.0012(4) | 0.0001(4) |
| C(11) | 4*e* | 0.1622(1) | 0.7471(1) | –0.15444(5) | 0.0230(5) | 0.0239(5) | 0.0179(5) | –0.0044(4) | –0.0024(4) | 0.0026(4) |
| C(12) | 4*e* | 0.0666(1) | 0.8412(1) | –0.18050(6) | 0.0283(6) | 0.0299(6) | 0.0270(6) | 0.0011(5) | –0.0018(4) | 0.0048(5) |
| C(13) | 4*e* | 0.0662(1) | 0.8786(2) | –0.25133(7) | 0.0376(7) | 0.0353(7) | 0.0312(6) | –0.0024(5) | –0.0087(5) | 0.0127(5) |
| C(14) | 4*e* | 0.1603(1) | 0.8253(2) | –0.29608(7) | 0.0450(7) | 0.0413(7) | 0.0218(5) | –0.0104(6) | –0.0036(5) | 0.0103(5) |
| C(15) | 4*e* | 0.2559(1) | 0.7341(2) | –0.26932(6) | 0.0377(7) | 0.0459(7) | 0.0214(5) | –0.0039(6) | 0.0056(5) | 0.0040(5) |
| C(16) | 4*e* | 0.2581(1) | 0.6942(1) | –0.19878(6) | 0.0278(6) | 0.0351(6) | 0.0218(5) | 0.0003(5) | 0.0014(4) | 0.0032(4) |
| C(21) | 4*e* | 0.1990(1) | 0.5909(1) | 0.15778(5) | 0.0186(4) | 0.0233(5) | 0.0171(4) | 0.0014(4) | –0.0003(4) | 0.0024(4) |
| C(22) | 4*e* | 0.1100(1) | 0.4888(1) | 0.18009(6) | 0.0292(6) | 0.0273(6) | 0.0263(6) | –0.0057(4) | 0.0047(4) | –0.0008(4) |
| C(23) | 4*e* | 0.0457(1) | 0.5059(1) | 0.24367(7) | 0.0302(6) | 0.0408(7) | 0.0288(6) | –0.0087(5) | 0.0079(5) | 0.0050(5) |
| C(24) | 4*e* | 0.0693(1) | 0.6253(2) | 0.28419(6) | 0.0320(6) | 0.0511(8) | 0.0207(5) | –0.0001(6) | 0.0065(4) | –0.0012(5) |
| C(25) | 4*e* | 0.1590(1) | 0.7268(2) | 0.26267(7) | 0.0453(7) | 0.0407(7) | 0.0254(6) | –0.0064(6) | 0.0052(5) | –0.0109(5) |
| C(26) | 4*e* | 0.2252(1) | 0.7089(1) | 0.19972(6) | 0.0352(6) | 0.0313(6) | 0.0246(5) | –0.0098(5) | 0.0044(5) | –0.0027(5) |
| C(31) | 4*e* | 0.3583(1) | 0.2231(1) | 0.01748(6) | 0.0336(6) | 0.0263(6) | 0.0281(6) | –0.0020(5) | –0.0053(5) | 0.0001(5) |
| C(32) | 4*e* | 0.3481(2) | 0.0215(2) | –0.06152(9) | 0.062(1) | 0.0322(7) | 0.0495(9) | –0.0053(7) | –0.0047(8) | –0.0113(6) |
| C(33) | 4*e* | 0.2407(2) | 0.0124(2) | 0.0551(1) | 0.068(1) | 0.0410(9) | 0.061(1) | –0.0219(8) | 0.0059(9) | 0.0091(7) |

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