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Three-dimensional hydrogen bonding network in the structures of (dimethylcyanamide)cobalt(II) complexes

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ABSTRACT

Two complexes *trans*-$[Co(NCNMe_2)_2(H_2O)_4]X_2{\cdot}2H_2O$ ($[\mathbf{1}]X_2{\cdot}2H_2O$; X = Cl, Br) were prepared by the reaction of $CoX_2{\cdot}6H_2O$ with 2 equiv of $NCNMe_2$ in methanol and isolated in excellent (98%) yields. The complexes were characterized by elemental analyses (C, H, N), high resolution ESI, IR spectroscopies, and their molecular structures were determined by a single-crystal X-ray diffraction. In $[\mathbf{1}]X_2{\cdot}2H_2O$, the hydrogen bonding between the counterions X^- and both ligated and crystallization water molecules responsible for the formation of a 3D-network. Based on quantum chemical DFT calculations and topological analysis of the electron density distribution within the formalism of Bader's theory (AIM method) these interactions can be classified as weak ($HO{-}H{\cdots}X^-$, $X^-{\cdots}H{-}OH$, and $HO{-}H{\cdots}X^-$ contacts, 2.5–3.5 kcal/mol) and moderate ($HO{-}H{\cdots}OH_2$ contacts, 5.7–6.3 kcal/mol) strength hydrogen bonds mainly due to electrostatics.

1. Introduction

Transition metal dialkylcyanamide complexes attract significant interest for the past decade due to diverse reactivity patterns of $NCNAlk_2$ ligands, which in many instances differ from those known for conventional nitrile NCR (R = Alk, Ar) metal-bound species [1]. Recent reports on the structural features and reactivity of the late transition metal dialkylcyanamide complexes were focused on the nickel [2–8] and iron [9–12] triads and no attention was paid to the cobalt triad. Few earlier works were devoted to the synthesis and reactivity of the cobalt(III) complexes featuring dialkylcyanamides [13–15] and only one paper [16] reported the generation of cobalt(II) complexes, where brutto-composition for all compounds was solely estimated and no structural data were provided [16]. Herein we describe the synthesis and X-ray structural studies of two novel (dimethylcyanamide)Co^{II} complexes. In the crystal structures, a 3D hydrogen bonding networks was identified and studied by using quantum chemical DFT calculations and topological analysis of the electron density distribution within the formalism of Bader's theory (AIM method).

2. Experimental

Dimethylcyanamide $NCNMe_2$ and the salts $CoX_2{\cdot}6H_2O$ (X = Cl, Br) were purchased from commercial sources and used as received. Electrospray ionization mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with an electrospray ionization (ESI) source. The instrument was operated in positive ion modes using a *m*/*z* range of 50–3000. The capillary voltage of the ion source was set at −4500 V (ESI^+-MS) and the capillary exit at +100 V. For ESI species were dissolved in MeOH. Infrared spectra (4000–400 cm^{-1}) were recorded on a Shimadzu IR Prestige-21 instrument in KBr pellets. Differential thermal analysis was performed with a NETZSCH TG 209 F1 Libra thermoanalyzer and MnO_2 powder being used as standard. The initial weights of the samples were in the range 1.5–2.0 mg. The experiments were run in an open alumina crucible in a stream of argon at a heating rate of 10 K/min. The final temperature of the experiments is 600 °C. Analysis of the thermal data was performed with Proteus analysis software.

2.1. Synthetic work

2.1.1. Synthesis of trans-$[Co(NCNMe_2)_2(H_2O)_4]X_2{\cdot}2H_2O$ ($[\mathbf{1}]Cl_2{\cdot}2H_2O$, $[\mathbf{1}]Br_2{\cdot}2H_2O$)

$CoX_2{\cdot}6H_2O$ (X = Cl, Br; 0.5 mmol, 118 and 163 mg, correspondingly) was dissolved in MeOH (3 mL), then $NCNMe_2$ (1 mmol, 70 mg) was added to the solution, whereupon color gradually turns from pink to blue. The reaction mixture was kept at 50 °C for 2 h in a closed flask without stirring and then at 20–25 °C for 20 h in air for slow evaporation until the solution was evaporated to *ca.* 0.2 mL and blue crystals were released. The crystalline product was separated by filtration, washed with Et_2O (five 3-mL portions) and dried in a desiccator over $CaCl_2$.

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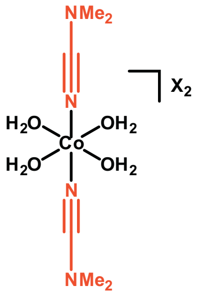
Table 1
Crystal data and structure refinement for *trans*-[**1**]$Cl_2·2H_2O$ and *trans*-[**1**]$Br_2·2H_2O$.

Identification code	[**1**]$Cl_2·2H_2O$	[**1**]$Br_2·2H_2O$
Empirical formula	$C_6H_{24}Cl_2CoN_4O_6$	$C_6H_{24}Br_2CoN_4O_6$
Formula weight	378.12	467.04
T (K)	100.01(10)	100(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	$Cmcm$
a (Å)	6.7374(3)	14.9975(8)
b (Å)	14.4803(6)	9.2451(7)
c (Å)	9.0914(4)	13.8552(8)
α (°)	90.00	90.00
β (°)	101.792(5)	90.00
γ (°)	90.00	90.00
V (Å^3)	868.23(7)	1921.1(2)
Z	2	4
ρ_{calc} (g/cm^3)	1.446	1.615
μ (mm^{-1})	10.815	5.074
F(000)	394.0	932.0
Crystal size (mm)	0.26 × 0.16 × 0.12	0.28 × 0.16 × 0.08
2θ range for data collection (°)	11.68–139.98	5.18–55
Index ranges	$-8 \leqslant h \leqslant 8$, $-16 \leqslant k \leqslant 17$, $-10 \leqslant l \leqslant 11$	$-7 \leqslant h \leqslant 19$, $-7 \leqslant k \leqslant 12$, $-18 \leqslant l \leqslant 10$
Reflections collected	4895	2822
Independent reflections	1640 [R_{int} = 0.0611]	1189 [R_{int} = 0.0316, R_{sigma} = 0.0310]
Data/restraints/parameters	1640/0/80	1189/0/62
Goodness-of-fit (GOF) on F^2	1.041	1.025
Final R indexes [$I \geqslant 2\sigma(I)$]	[a]R_1 = 0.0680, [b]wR_2 = 0.1820	R_1 = 0.0231, wR_2 = 0.0498
Final R indexes [all data]	R_1 = 0.0745, wR_2 = 0.1902	R_1 = 0.0280, wR_2 = 0.0519
Largest difference peak and hole (e Å^{-3})	1.25 and −1.22	0.50 and −0.32

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.



[**1**]X_2 (X = Cl, Br)

Fig. 1. Graphical representation of the (dimethylcyanamide)Co^{II} complexes.

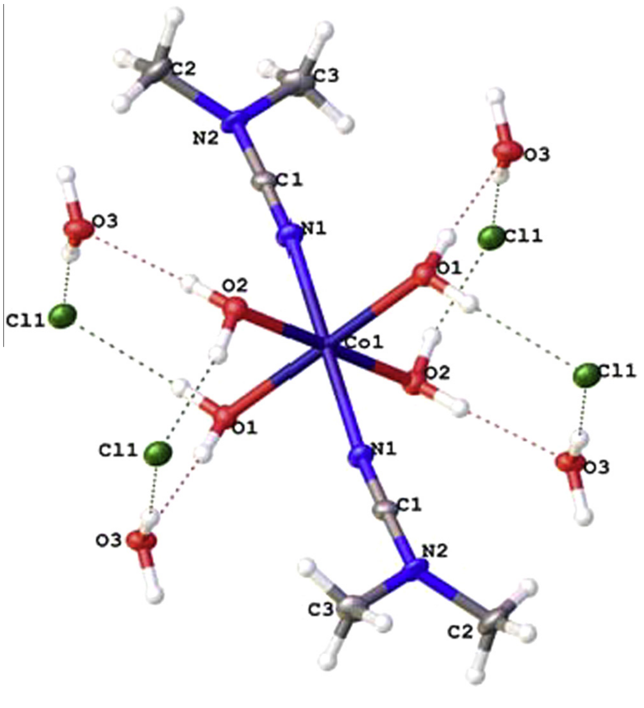


Fig. 2. Molecular structure of *trans*-[**1**]$Cl_2·2H_2O$ with the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

2.1.2. *trans-[Co(NCNMe$_2$)$_2$(H$_2$O)$_4$]Cl$_2$·2H$_2$O*

184 mg, 98%. *Anal.* Calc. for $C_6H_{24}N_4Cl_2CoO_6$: C, 19.06; H, 6.04; N, 14.82. Found: C, 19.32; H, 4.99; N, 15.07%. HRESI$^+$, *m/z*: 134.5467 ($[M-2Cl-2H]^{2+}$ requires 134.5325), 163.9551 ($[M-NCNMe_2-Cl-4H_2O]^+$ requires 163.9551), 234.0094 ($[M-Cl-4H_2O]^+$ requires 234.0082), 252.0188 ($[M-Cl-3H_2O]^+$ requires 252.0188). ν_{max} (KBr)/cm^{-1}: 3390 m ν(O–H), 2948, 2938 w ν(C–H), 2262 m ν(C≡N), 1622 $\delta_w(H_2O)$.

2.1.3. *trans-[Co(NCNMe$_2$)$_2$(H$_2$O)$_4$]Br$_2$·2H$_2$O*

229 mg, 98%. *Anal.* Calc. for $C_6H_{24}N_4Br_2CoO_6$: C, 15.43; H, 5.18; N, 12.00. Found: C, 15.62; H, 3.98; N, 12.15%. HRESI$^+$, *m/z*: 134.5493 ($[M-2Cl-2H]^{2+}$ requires 134.5325), 207.9084 ($[M-NCNMe_2-Br-4H_2O]^+$ requires 207.9046), 277.9629 ($[M-Br-4H_2O]^+$ requires 277.9377). ν_{max} (KBr)/cm^{-1}: 3328 m ν (O–H), 2936 w ν(C–H), 2266 m ν(C≡N), 1634 $\delta_w(H_2O)$.

2.2. *Computational details*

The single point calculations for model clusters Co–Br, Co–Cl, Ni–Br, and Ni–Cl have been carried out at the DFT level of theory using the M06 functional (this functional describes reasonably weak dispersion forces and non-covalent interactions) [17] with the help of GAUSSIAN-09 program package [18]. Unrestricted approximations for the structures with open electron shells were employed. The experimental X-ray geometries were used as starting points. The calculations were carried out using a multi electron fit fully relativistic energy-consistent pseudopotentials MDF10 of the Stuttgart/Cologne group that described 10 core electrons and the appropriate contracted basis sets for the cobalt and nickel atom