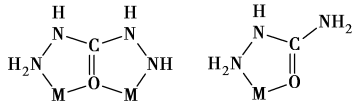
文章编号：1006-9941(2006)06-0491-01

Two Coordination Compounds Using Semicarbazide (SCZ) as Bidentate Ligands: $[Ni(SCZ)_3](NO_3)_2$ and $Cu(SCZ)_2Cl_2$

GUO Jin-yu, ZHANG Tong-lai, MA Gui-xia, ZHANG Jian-guo, LIU Yan-hong

(*State Key Laboratory of Explosion Science and Technology at Beijing Institute of Technology, Beijing* 100081, *China*)

Recently one derivative of carbohydrazide (CHZ)-semicarbazide (SCZ) has attracted researchers' attention on the way to synthesize new kinds of complex energetic materials. When coordinated to metal centers, semicarbazide uses similar coordination patterns as carbohydrazide-form the 5-member ring system by means of oxygen and terminal nitrogen atoms as scheme 1.



Scheme 1 The 5-member ring coordination patterns of CHZ and SCZ

In this paper, two kinds of coordination compounds have been prepared by direct methods using semicarbazide as starting material. Their crystals were cultured at room atmosphere and their structures demonstrated using X-ray single crystal diffraction. $[Ni(SCZ)_3](NO_3)_2$ crystallized into monoclinic, $P2(1)/c$ space group, with cell parameters of $a = 1.0832(2)$ nm, $b = 0.9980(2)$ nm, $c = 1.3801(3)$ nm, $\beta = 102.89(3)°$. $M_r = 407.97$, $V = 1.4543(5)$ nm^3, $Z = 4$, $D_c = 1.863$ Mg·m^{-3}, $\mu = 1.409$ mm^{-1}, $F(000) = 840$, $S = 0.993$. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0359$, $wR_2 = 0.0877$, R indices for all data: $R_1 = 0.0445$, $wR_2 = 0.0906$. $Cu(SCZ)_2Cl_2$ crystallized into monoclinic, $P2(1)/c$ space group, with cell parameters of $a = 0.7555(2)$ nm, $b = 0.9295(2)$ nm, $c = 0.6888(1)$ nm, $\beta = 101.45(0)°$. $M_r = 284.60$, $V = 0.4740(2)$ nm^3, $Z = 2$, $D_c = 1.994$ Mg·m^{-3}, $\mu = 2.847$ mm^{-1}, $F(000) = 286$, $S = 1.112$. Final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0229$, $wR_2 = 0.0584$, R indices for all data: $R_1 = 0.0265$, $wR_2 = 0.0600$. Anal. calcd. for $C_3H_{15}N_{11}NiO_9$ (%): C 8.83, H 3.71, N 37.77; found (%): C 8.75, H 3.80, N 37.73. Anal calcd. for $C_2H_{10}Cl_2CuN_6O_2$ (%): C 8.44, H 3.54, N 29.53; found (%): C 8.39, H 3.58, N 29.57. FTIR (ν, KBr, cm^{-1}): 3470s, 3368s, 3324s, 3210s, 1657vs, 1386vs for $[Ni(SCZ)_3](NO_3)_2$; 3474s, 3371s, 3252s, 3150s, 1663vs for $Cu(SCZ)_2Cl_2$. In $[Ni(SCZ)_3](NO_3)_2$, Ni(II) center is hexa-coordinated by three semicarbazides (bidentate, by means of O and N) while in $Cu(SCZ)_2Cl_2$, Cu(II) center is hexa-coordinated by two semicarbazide (bidentate) and two chlorate to form the lightly distorted octahedra. In both compounds, semicarbazides coordinate to Ni(II) or Cu(II) centers to form the 5-member ring system. With the intermolecular hydrogen bonds, molecules are linked together to form the three-dimensional packing diagrams in both compounds. Thermal analyses DSC and TG-DTG together with the FTIR spectra have been performed on both compounds to investigate their thermal decomposition mechanisms. For $[Ni(SCZ)_3](NO_3)_2$, from 484 to 573 K (43.64%) is the loss of the two NO_3^{2-} groups and the change of $[Ni(SCZ)_3]^{2+}$ to nickel complex with —CO—NH— group; from 573 to 624 K (30.57%) is the decomposition of the compound. The composition of the residues (20.08%) can be assigned to be Ni_2O_3 (calcd. 20.27%). For $Cu(SCZ)_2Cl_2$, it decomposes continuously and completely from 433 to 723 K. The final residues (26.06%) got 723 K are assigned to be CuO (calcd. 27.95%).

Key words: physical chemistry; coordination compound; crystal structure; semicarbazide; thermal decomposition mechanism

CLC number: O614; TJ55

Received Date: 2006-09-06; **Revised Date**: 2006-11-13

Project Supported: The National Natural Science Foundation of China (20471008) and The Fundamental Research Foundation of Beijing Institute of Technology (BIT-UBF-200502B4221)

Biography: GUO Jinyu, (1979 -), male, Ph. D., Research field: energetic materials. e-mail: goldfish@bit.edu.cn