

三乙基黄原酸镍(II)四甲胺盐的晶体结构

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关键词: 乙基黄原酸 镍酸盐(II) 晶体结构
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Crystal Structure of Tetramethylammonium Tris(ethylxanthato)nickelate(II)

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An unexpected but welcome compound **1** obtained through organic synthesis, can find a lot of applications in electrochemistry, industrial extracting agent for gold and antiwear additive in lubricating oil. The Ni center in compound **1** has an octahedral geometry with a tetramethylammonium cation as a charge balance. CCDC: 252203.

Keywords: ethylxanthato nickelate(II) crystal structure

Comment

During the past three decades, the chemistry of trivalent nickel coordinated to nitrogen and/or oxygen donor ligands has received much attention^[1,2]. In contrast, the nickel(III) chemistry of classical sulfur donor ligands has made tardy progress. Chakravorty et al. did many research in this field^[3], including nickel(II) precursors, synthesis and their electrochemistry properties. Recently, we performed the reaction of H-Norf (norfloxacin) with carbon sulfide and potassium hydroxide in ethanol solution at 273 K, then nickel acetate was added into the above mixed solution, stirred until the solution is clear. Let the solution evaporate in air for about one week, the dark-green crystals were obtained (Scheme 1). As indicated in Scheme 1, we

failed to get the expected product instead of an unexpected but welcome product. Since metal-sulfur interaction is anticipated to be stronger in Co (alkylxanthato)₃, than in Ni(alkylxanthato)₂ in which ligand oxidation in the latter may be expected to occur at a comparably lower electrochemical potential. Thus, the product is available for the electrochemistry study. On the other hand, the coordination compound **1** formed by xanthato ligands is probably candidate material for antiwear additive in lubricating oil and industrial extracting agent for gold. Herein we report its synthesis and single crystal structure.

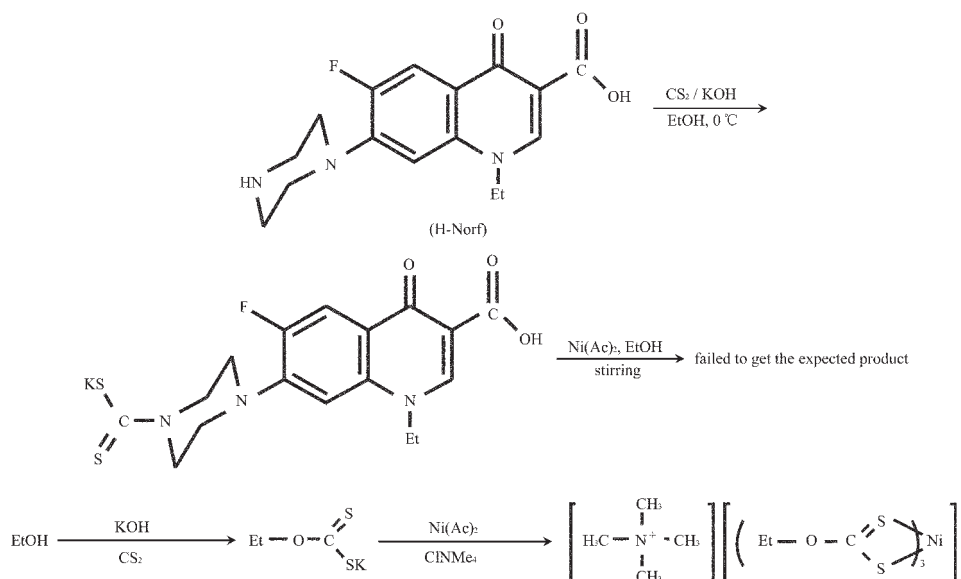
The solid state structure of compound **1** [tetramethylammonium tris(ethylxanthato)-nickelate(II)] determined by X-ray diffraction, reveals that the coordina-

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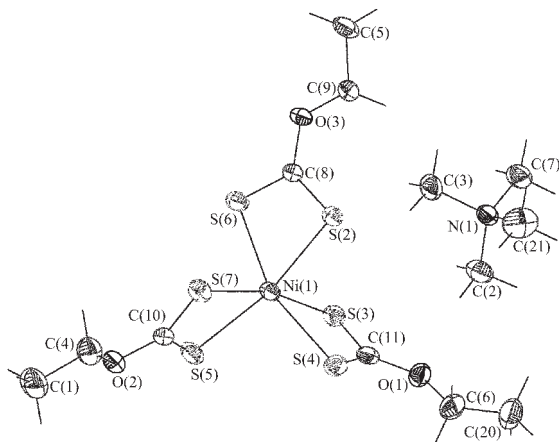
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Scheme 1 Synthesis of $[\text{Ni}(\text{EtOCS}_2)_3][\text{N}(\text{CH}_3)_4]$ (**1**)

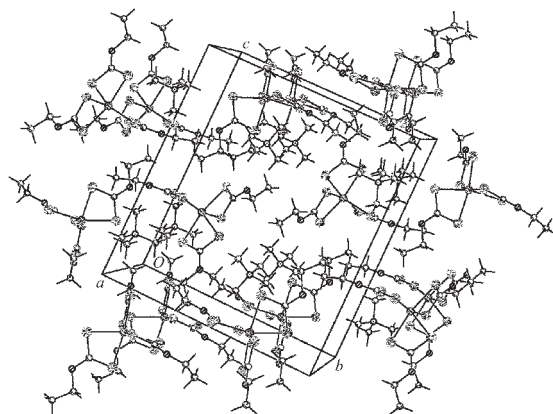
tion environment around Ni center can be best described as a significantly distorted octahedron in which ethylxanthato ligand acts as bidentate chelating agent as shown in Fig.1. Fig.2 shows its crystal pack-

Fig.1 ORTEP view (20% probability ellipsoids) of $[\text{Ni}(\text{EtOCS}_2)_3][\text{N}(\text{CH}_3)_4]$ (**1**)

Key bond distances and angles(nm, °):

Ni(1)-S(5) 0.239 3(17); Ni(1)-S(3) 0.241 8(2);
 Ni(1)-S(6) 0.242 7(16); Ni(1)-S(2) 0.243 0(17);
 Ni(1)-S(4) 0.244 3(18); Ni(1)-S(7) 0.245 6(2);
 S(5)-Ni(1)-S(3) 96.93(7); S(5)-Ni(1)-S(6) 99.92(6);
 S(3)-Ni(1)-S(6) 95.23(7); S(5)-Ni(1)-S(2) 167.38(7);
 S(3)-Ni(1)-S(2) 94.21(6); S(6)-Ni(1)-S(2) 73.11(5);
 S(5)-Ni(1)-S(4) 98.22(6); S(3)-Ni(1)-S(4) 73.25(6);
 S(6)-Ni(1)-S(4) 159.57(6); S(2)-Ni(1)-S(4) 90.62(6);
 S(5)-Ni(1)-S(7) 72.90(7); S(3)-Ni(1)-S(7) 166.55(6);
 S(6)-Ni(1)-S(7) 95.19(7); S(2)-Ni(1)-S(7) 96.92(6);
 S(4)-Ni(1)-S(7) 99.05(7)

ing mode. Moreover, the Ni center is coordinated to six sulfur atoms that come from three xanthato ligands respectively, which forms three independent four-membered rings. The NiS_6 coordination polyhedron shows large distortions from ideal octahedral geometry, much of which originates from the acute chelate bite angles. The polyhedron has an approximate 3-fold symmetry. The distance of Ni-S (shown in Fig.1) is in the range of 0.239 3 to 0.245 6 nm, which is longer than that found in bis (O-3,3-dimethylbutylxanthato-S,S')-nickel (II) (0.220 3 and 0.221 6 nm)^[4], but shorter than that found in tetraethylammonium rac-tris(benzothiazoline-2-thionato-N,S)-nickel(II)(0.253 3, 0.258 8 and 0.254 4 nm)^[5]. Finally, the bond lengths of C-C, C-O, C-N, and C-S are unexceptional.

Fig.2 Packing perspective view of $[\text{Ni}(\text{EtOCS}_2)_3][\text{N}(\text{CH}_3)_4]$ (**1**) along *a*-axis

Experimental

Intensity data were collected at 293 (2) K on a Bruker AXS SMART CCD. $\text{C}_{13}\text{H}_{27}\text{NNiO}_3\text{S}_6$, $M=496.43$, monoclinic, space group $P2_1/n$, $a=0.873\ 2(3)$, $b=1.574\ 9(5)$, $c=1.717\ 3(6)$ nm, $\beta=97.432(6)^\circ$, $V=2.341\ 7(14)$ nm³, $Z=4$, $\theta_{\text{max}}=28.46$, $R=0.070\ 7$ (4 104 data with $I \geq 2\sigma(I)$), $R=0.115\ 7$ (all data; 11 675). Programs used: SAINT, SADABS, SHELX-97, ORTEP.

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