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Inorganic Chemistry Communications 8 (2005) 463–466

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Thiodiacetate cobalt(II) complexes: Synthesis, structure and properties

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Received 15 February 2005; accepted 27 February 2005
Available online 23 MArch 2005

Abstract

The novel cobalt thiodiacetate complex $[Co(tda)(H_2O)]_n$ (**1a**) (tda = $S(CH_2COO)_2^{2-}$) was synthesized from the reaction of aqueous solutions of cobalt dichloride with a 1:1 mixture of Na_2CO_3 and thiodiacetic acid. A second isomer was also obtained occasionally and identified as complex $[Co(tda)(H_2O)_3]$ (**1b**). The reaction of **1a** with 2,2′-bipyridine (bipy) gave compound $[Co(tda)(bipy)(H_2O)] \cdot 4H_2O$ (**2**), which has been structurally characterized and represents, to our knowledge, the first X-ray determination of a thiodiacetate–cobalt complex. The coordination is monomeric pseudo-octahedral as determined by the typical tridentate thiodiacetate ligand with a facial configuration, the chelate bipy ligand and one water molecule. Conversely, the interaction of bis(2-pyridyl)ketone with **1a** afforded the compound $[Co\{OC(OH)(2\text{-pyridyl})_2\}_2]^+[Htda]^- \cdot 3H_2O$ (**3**), as confirmed from an X-ray analysis. The bis(2-pyridyl)ketone ligand is hydrolyzed with a concomitant oxidation of the metal to Co(III), a process which has been previously described, while the tda ligand, displaced from the coordination sphere, is monoprotonated and acts as counterion.

Keywords: Cobalt(II); Thiodiacetate; Thiodiglycolate; Crystal structure

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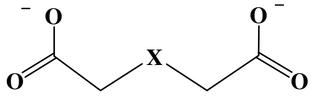
The chemistry of thiodiacetate (tda) transition metal complexes is comparatively less developed than that of the related oxydiacetate (oda) complexes (see **I**), as confirmed by the definitely smaller number of tda X-ray structures contained in the CCDC [1]. For instance, amongst the metals of the first transition row, oda complexes are known for titanium [2], vanadium [3], manganese [4], iron [5], cobalt [6], nickel [7], copper [8] and zinc [9]. In contrast, tda complexes have been characterized only for manganese [10], nickel [11], copper [12] and zinc [13]. Recently, Niclós-Gutiérrez and coworkers [14] have briefly reviewed the structural features of the known tda complexes.



X= O, oda; S, tda

I

Due to our continuous interest for the ligands oda [3,4a,5a,6b] and tda [10a], we planned to explore the behaviour of the latter toward cobalt, since in the literature there is only one reference to a tda–Co(II) species which is limited in particular to its behaviour in solution [15]. In this communication, we present some preliminary

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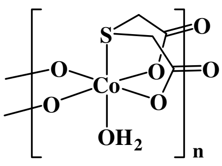
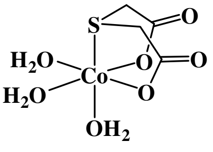
doi:10.1016/j.inoche.2005.02.011

results on the preparation and X-ray characterization of the new tda–cobalt complexes.

Treatment of aqueous solutions of cobalt dichloride with a 1:1 mixture of Na_2CO_3 and thiodiacetic acid, $S(CH_2COOH)_2$, affords, after the appropriate work up, dark pink microcrystals of the complex $[Co(tda)(H_2O)]_n$ (**1a**), in good yields [16]. A closely related thiodiacetate complex of manganese could be prepared by following a similar experimental procedure [10a]. Also, the complex $[Ni(tda)(H_2O)_3]$, already reported by Kopel et al. [11a] and Niclós-Gutiérrez and coworkers [14], may be synthesized by this route. Compound **1a** is air stable and soluble in water, but not in solvents of low polarity. Its IR spectrum displays a very strong and broad absorption band at about 1589 cm^{-1}, which corresponds to the antisymmetric vibrations of the tda carboxylate groups. Another strong band at 1399 cm^{-1} is assigned to the corresponding symmetric vibrations (for an analysis of the IR bands of thiodiacetate see [17]). The IR spectrum is identical to that of the structurally characterized polymeric complex $[Cd(tda)(H_2O)]_n$ [18] and, consequently, we proposed a similar crystalline structure for **1a**. During the preparation of **1a**, occasionally some dark pink crystals, differently shaped as needles, were also observed. The IR spectrum of this second compound, **1b**, showed only some minor differences, mainly in the region of coordinated water. Essentially, the spectrum is identical to that of the compound $[Ni(tda)(H_2O)_3]$ and, also on the basis of analytical data, the formula of **1b** is suggested to be $[Co(tda)(H_2O)_3]$. The presence of a related behaviour in the related oxydiacetate cobalt complexes has been recently described [19].



1a



1b

The reaction of aqueous solutions of compound **1a** with 2,2′-bipyridine (bipy) gives a new complex, which can be isolated in good yields as the crystalline solid $[Co(tda)(bipy)(H_2O)] \cdot 4H_2O$ (**2**) [20]. Two broad absorptions for the tda carboxylate groups are found in the IR spectrum at 1599 and 1400 cm^{-1}, respectively. The effective magnetic moment (measured for **2** in the solid state and at room temperature) is 4.54 μ_B, a value which is typical of high-spin mononuclear d^7-cobalt compounds (see for example [21]). The crystal structure of **2** has been determined by X-ray diffraction methods [22] and represents, at the best of our knowledge, the first thiodiacetate–cobalt complex, which is structurally characterized. The coordination polyhedron around the cobalt atom is a distorted octahedron in which the central metal atom is coordinated by the tridentate tda ligand in its typical *fac*-arrangement. The coordination sphere is completed by the bidentate bipy ligand and one water molecule, *trans* to the sulphur donor atom of tda (Fig. 1).

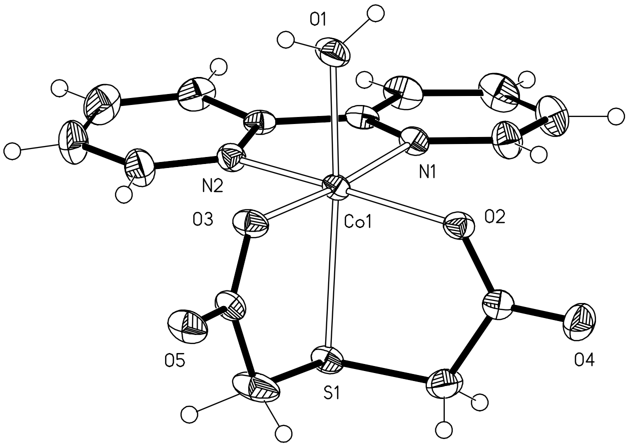


Fig. 1. Molecular structure of **2**. Crystallization water molecules are not shown. Selected bond distances (Å) and angles (°): Co(1)–O(3) 2.029(2), Co(1)–O(2) 2.046(2), Co(1)–S(1) 2.508(1), Co(1)–O(1) 2.091(2), Co(1)–N(1) 2.155(2), Co(1)–N(2) 2.110(2), O(3)–Co(1)–O(2) 96.56(7), O(3)–Co(1)–N(2) 97.83(7), O(2)–Co(1)–N(2) 163.56(7), O(3)–Co(1)–N(1) 173.82(7), O(2)–Co(1)–N(1) 89.49(7), O(1)–Co(1)–N(1) 92.41(7), O(3)–Co(1)–S(1) 81.83(5), O(2)–Co(1)–S(1) 82.02(5), N(2)–Co(1)–S(1) 92.18(6), N(1)–Co(1)–S(1) 100.33(5).

Complex **2** is isomorphous with the known nickel [11a], zinc [13b] and copper analogues [12b]. The M–O, M–S and M–N bond lengths in the four compounds are conveniently reported in Table 1. In spite of the full comparability, the trends based on the radii and the progressively higher electron population of the M(II) ions are not straightforward. In any case, the most contracted and symmetrical coordination sphere seems to be that of nickel with its $t_{2g}^6e_g^2$ electron configuration. The cobalt ion ($t_{2g}^5e_g^2$) shows significantly longer metal–bipyridine distances probably on account of the reduced π-backbonding capability from one half filled t_{2g} level (d_{xz} or $d_{yz} \rightarrow$ bipy π* level). Cu(II) shows the expected equatorial contraction/axial elongation (the Cu–S and C–O_w distances are the longest in the series), which may be interpreted in terms of Jahn–Teller effect ($t_{2g}^6e_g^3$ configuration). Finally, the d^{10} Zn(II) complex is an

Table 1
Comparison of selected bond distances (Å) around the metal centre in $[M(tda)(bipy)(H_2O)] \cdot 4H_2O$ complexes

	Co, **2**	Ni [11a]	Zn [13b]	Cu [12b]
M–O	2.029(2)	2.016(2)	2.047(2)	1.973(4)
	2.046(2)	2.036(2)	2.067(2)	1.977(4)
M–S	2.508(1)	2.423(2)	2.618(1)	2.697(1)
M–N	2.155(2)	2.042(3)	2.124(2)	2.019(4)
	2.110(2)	2.071(3)	2.167(2)	2.024(4)
M–O_w	2.091(2)	2.046(2)	2.064(2)	2.353(3)