

Transition metal derivatives of 1,10-phenanthroline-5,6-dione: Controlled growth of coordination polynuclear derivatives

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Abstract

The synthesis and the characterization of several mono- and polynuclear derivatives of 1,10-phenanthroline-5,6-dione (**1**) are presented. The reaction of **1** with $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}$) gives compounds of general formula $M(\text{O}, \text{O}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2)_3$, $M = \text{Cr}$ (**2**), Mo (**3**). Compound **3** is also obtained starting from $\text{Mo}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$, whereas the reaction of $\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2$ with **1** affords the ionic derivative $[\text{Cr}(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)_2][\text{C}_{12}\text{H}_6\text{N}_2\text{O}_2]$ (**4**), which has been studied by EPR spectroscopy and DFT calculations. $\text{FeCl}_2(\text{N}, \text{N}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2)_2$ (**6**), is obtained by thermal decomposition of $[\text{Fe}(\text{N}, \text{N}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2)_3]\text{Cl}_2$ (**5**). Polynuclear compounds of general formula $\text{Cr}[\text{O}, \text{O}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2\text{-N}, \text{N}'\text{-MCl}_4]_3$, containing chromium and a Group 4 element $M = \text{Ti}$ (**7**), Zr (**8**), Hf (**9**), are prepared from $\text{Cr}(\text{O}, \text{O}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2)_3$ and the corresponding MCl_4 or MCl_4DME . Polynuclear derivatives of iron and chromium of formula $[\text{Fe}(\text{N}, \text{N}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2\text{-O}, \text{O}'\text{-CrCl}_2(\text{THF})_2)_3][\text{PF}_6]_2$ (**10**), and $\text{Cr}[\text{O}, \text{O}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2\text{-N}, \text{N}'\text{-FeCl}_2(\text{THF})_3]$ (**11**), are obtained by the reaction of $[\text{Fe}(\text{N}, \text{N}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2)_3][\text{PF}_6]_2$ with three equivalents of $\text{CrCl}_2(\text{THF})_2$ and from $\text{Cr}(\text{O}, \text{O}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2)_3$ and $\text{FeCl}_2(\text{THF})_{1.5}$, respectively. Compound **11** reacts with **1** (3 equivalents in *sym*- $\text{C}_2\text{H}_2\text{Cl}_4$ or 6 equivalents in ethanol) to give $\text{Cr}[\text{O}, \text{O}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2\text{-N}, \text{N}'\text{-FeCl}_2(\text{N}, \text{N}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2)_3]$ (**12**), and $[\text{Cr}(\text{O}, \text{O}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2\text{-N}, \text{N}'\text{-Fe}(\text{N}, \text{N}'\text{-C}_{12}\text{H}_6\text{N}_2\text{O}_2)_2)_3]\text{Cl}_6$ (**13**), respectively.

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1. Introduction

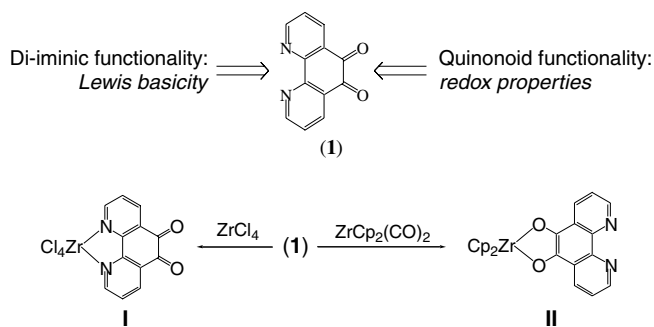
1,10-Phenanthroline-5,6-dione (**1**), is a versatile molecule with applications in organic [1] and biological [2] chemistry, and in the synthesis of materials showing interesting optical [3] or electrical properties [4].

In the recent years, some studies have dealt with the coordination properties of **1** towards both early and late transition metals and lanthanides [3,5]. Compound **1** shows indeed a peculiar reactivity due to the presence of two reactive sites: the quinonoid- and the di-iminic functions. This versatile behaviour is exemplified by the reaction of **1** with

ZrCl_4 or $\text{ZrCp}_2(\text{CO})_2$, where the change in the coordination environment around zirconium allows the isolation of *O, O'*- or *N, N'*-coordinated compounds, see Scheme 1 [5e,5g].

It has to be noted that when **1** coordinates through the nitrogen atoms, the entire complex, **I**-type, may be used as “quinone equivalent” in reactions with compounds containing metals in a low oxidation state. On the other hand, oxygen-bound complexes of 1,10-phenanthroline-5,6-dione, **II**-type, may be used as a “phenanthroline equivalent” ligand in reactions with Lewis acids. In both cases, the result is the formation of complexes of higher nuclearity. A close examination of the polynuclear systems reported in the literature [3,5g,6] has revealed that the synthetic strategies used to increase the nuclearity generally

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Scheme 1.

start from systems which contain inert fragments ML_n with L = reduced quinones, cyclopentadienyls, phosphines, and substituted bipyridyl, thus preventing the utilization of all the coordination sites for chain growing.

In this paper, we report on the preparation of some new chromium, molybdenum and iron complexes containing N,N' - or O,O' -coordinated **1**, which can be used to grow oligo- or heterometallic compounds containing **1** as a bridging ligand.

2. Results and discussion

Compound **1** has been obtained by a slight modification of the procedure reported by Yamada and co-workers [7] consisting of the addition of a H_2SO_4/HNO_3 mixture, cooled at ca. $-78^\circ C$, to solid 1,10-phenanthroline and KBr . Particular care is required during the neutralization of the highly acidic reaction mixture due to the known [1a,1b] alkaline decomposition of **1** to 4,5-diazafluoren-9-one. By operating as reported in Section 4, reproducible yields as high as 70% of recrystallized **1** (from methanol) have been obtained.

2.1. Mononuclear derivatives

2.1.1. Chromium and molybdenum

Recent contributions from our and other laboratories have described the use of transition metal complexes containing elements in low oxidation state as precursors to organometallic, inorganic and coordination compounds [8]. As far as quinone derivatives are concerned, metal carbonyls of general formula $M(CO)_n$, $M = V, Cr, Mo, W$, $n = 6$; $M = Fe$, $n = 5$, have been used to obtain compounds of general formula $M(\text{quinone})_x$ [9]. Also the highly reactive $M(\eta^6\text{-arene})_2$ derivatives have had some synthetic application [10,11], but their use is limited due to the lower availability of the arene derivatives with respect to the carbonyl ones.

In view of the fact that the preparation of quinone derivatives from low valent metal complexes is “the most convenient in terms of product isolation and purification” [9a], we chose $M(CO)_6$, $M = Cr, Mo$, as the starting material. The formation of a “phenanthroline equivalent” complex, able

to give polynuclear derivatives by reaction with halides of early and middle transition elements, was expected.

We have found that $Cr(CO)_6$ and $Mo(CO)_6$ react with **1** in mesitylene at $150^\circ C$ ($M = Cr$) or in refluxing toluene ($M = Mo$) affording compounds **2** and **3**, respectively; see Scheme 2.

By reacting $Cr(CO)_6$ and **1** in boiling anisole, the solvated $2 \cdot 3$ anisole complex is obtained,¹ which can be transformed in **2** by heating in the solid state at $150^\circ C/0.01$ mmHg.

Compounds **2** and **3** are rather insoluble in hydrocarbons and have only a moderate solubility in chlorinated hydrocarbons, THF and acetone.²

The IR spectra of both **2** and **3** show an absorption of medium intensity at about 1420 cm^{-1} [**2**, 1423; **3**, 1426], but in the case of **3** a rather intense absorption is observed at 1360 cm^{-1} . By taking into consideration that absorptions between 1500 and 1400 cm^{-1} are typical of the mono-reduced quinone (semiquinonate anion) and those between 1400 and 1300 cm^{-1} characterize the fully reduced quinonoid functionality [12,13], we propose that **2** is formally a chromium(III) derivative containing phenanthroline semiquinonato ligands. As far as **3** is concerned, mainly based on the similarities of the structural properties between 9,10-phenanthrenequinone derivatives and the coordination compounds of **1**, we suggest that the compound may be a derivative of molybdenum(V) with a coordinative situation similar to that observed for $Mo(C_{14}H_8O_2)_3$ [14], namely containing two diolate and one semiquinone groups.

Compound **3** is diamagnetic, suggesting the presence of strong antiferromagnetic coupling between the unpaired electrons of the monoelectronically reduced **1** and the molybdenum. Such a coupling is a rather common phenomenon within transition metal quinonoid derivatives: for instance, it has been observed in $M(\text{quinone})_3$ derivatives with $M = V, Cr, Fe$ [15].

On the other hand, the chromium derivative **2** is paramagnetic with a magnetic moment (3.41 BM at 298 K) in between the spin-only value for a system containing two (2.82 BM) and three (3.87 BM) unpaired electrons, thus suggesting a partial coupling between the electrons of chromium(III) of d^3 electronic configuration and three unpaired electrons of the monoelectronically reduced **1** ligands.

The reaction between $Mo(\eta^6\text{-CH}_3C_6H_5)_2$ and **1** proceeds with loss of the arene ligands (toluene is quantitatively found in solution by GC-MS) and affords compound **3** in good yields. On the other hand, no toluene is produced in the reaction of $Cr(\eta^6\text{-CH}_3C_6H_5)_2$ and **1**. The

¹ The presence of anisole in the compound was suggested by the IR absorption of the ether at 1598, 1496, 1245 and 754 cm^{-1} .

² Due to the retention of clathrated solvent when the compound crystallizes from either aromatic hydrocarbons (toluene) or basic media (acetone or THF) crystals rapidly deteriorate even under a solvent saturated atmosphere. This fact prevented the collection of X-ray data suitable for a crystal structure solution.

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