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Mo(IV) and W(IV) cyanido complexes with Schiff bases. Synthesis, X-ray single crystal structures, physicochemical properties and quantum chemical calculations

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ABSTRACT

In the reaction of salicylaldehyde derivatives and aminoethanol with Mo(IV) or W(IV) cyanido complexes, six new salts were isolated and characterized by physicochemical measurements. The single crystal X-ray analysis of four salts of the formula $(PPh_4)_2[M(CN)_3O(LL)]\cdot nH_2O$, (where LL = Schiff bases formed *in situ* in the reaction of aminoethanol and 5-bromo-, 5-chloro-, 5-methoxy-, 3,5-dichloro- or 5-bromo-3-methoxy-substituted salicylaldehyde, M = Mo or W, n = 1, 1.5, 2 or 5 water molecules) reveals a distorted octahedral geometry of the anions. All the complexes were characterized by elemental analysis, IR and UV–Vis spectroscopy and by cyclic voltammetry measurements. The role of the salicylaldehyde substituents on the structures and physicochemical properties is discussed. The results are compared with quantum chemical calculations, indicating that, contrary to literature data, even strong hydrogen bonds do not influence the anion structure.

1. Introduction

The structures of anions (or cations) of d-electron metal complexes are very often discussed in terms of ligand–metal interactions (for example the *trans* effect), but they also serve as an interesting source of information for the interactions of complex cations (or anions) with solvent molecules. During the last few years, much attention has been directed towards the syntheses of Mo(IV) and W(IV) oxido-cyanido complexes as these complexes are especially good for structure discussions due to their octahedral structures with fixed ligand positions [1]. In complexes with $[M(CN)_4OL]^{n-}$ anions (M = Mo or W, L denotes a monodentate ligand) the ligand L is always *trans* to the M═O bond. In complexes with $[Mo(CN)_3O(LL)]^{n-}$ anions (LL denotes a bidentate ligand) one end of LL ligand is also *trans* to the M═O bond, while the second donor atom is in a *cis* position. The stability of the complex structure is very promising for an investigation of the correlations between the structure and physicochemical properties.

The main problem is that for molybdenum(IV) and tungsten(IV) cyanido complexes only a few complexes are known, especially with organic ligands [2–20]. Many efforts were undertaken to synthesize new complexes of this type, but still less than 50 were known, until now. The number of crystal structures resolved is even smaller, which makes systematic comparisons not always possible. Thus, it is difficult to draw correlations between the ligand and physicochemical properties for a given complex. It is known, however, that complexes with the same anion and different cations show anion distortion, discussed mainly in terms of possible long range hydrogen interactions influencing the anion structure [1].

In this work we synthesized several new complexes of Mo(IV) and W(IV) with Schiff base ligands derived from salicylaldehyde and 2-aminoethanol. To study the small effects of ligand and solvent interactions we decided to use substituted salicylaldehydes. The selected Schiff bases are identical to those used by us for copper(II) complexes (with 5-chloro, 5-bromo and 5-bromo-3-methoxy substituents), but the list of substituents was increased to include 3,5-dichloro and 5-methoxy [21]. It has been found that small changes on these ligands can dramatically influence the long distance interactions for copper complexes, even by changing the copper coordination number, which was interpreted in terms of hydrogen bonding effects. However, for 4- and 5-d electron metals, the hydrogen bonding interactions may not be so important as is suggested for 3-d metals. We also carried out quantum chemical calculations for isolated complex anions to examine if the observed deformation of the Mo(IV) or W(IV) anion may be reproduced

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without considering the hydrogen bonding network present in the crystal structure.

2. Experimental

2.1. Materials and methods

$K_3Na[Mo(CN)_4O_2]\cdot 6H_2O$ and $K_3Na[W(CN)_4O_2]\cdot 6H_2O$ were synthesized according to the literature methods [22,16]. All other chemicals were of analytical grade (Aldrich) and were used as supplied. Microanalyses of carbon, hydrogen and nitrogen were performed using a Vario Micro Cube elemental analyzer. Solid samples for IR spectroscopy were compressed as KBr pellets and the IR spectra were recorded on a Bruker EQUINOX 55 FT-IR spectrophotometer. Electronic absorption spectra (qualitative) were measured with a Shimadzu UV–Vis–NIR UV-3600 spectrophotometer. Diffuse reflectance spectra were measured in $BaSO_4$ pellets with $BaSO_4$ as a reference using a Shimadzu UV-3600 equipped with an ISR-3100 attachment. Cyclic voltammetry measurements were carried out in DMSO (dimethyl sulfoxide) with $[Bu_4N]PF_6$ (0.10 M) as the supporting electrolyte, using Pt working and counter and Ag/AgCl reference electrodes on an AUTOLAB/PGSTAT 128 N Potentiostat/Galvanostat. $E_{1/2}$ values were calculated from the average anodic and cathodic peak potentials, $E_{1/2} = 0.5(Ea + Ec)$. The redox potentials were calibrated versus ferrocene (0.440 V versus SHE), which was used as an internal potential standard for measurements in organic solvents to avoid the influence of a liquid junction potential; the final values are reported versus the standard hydrogen electrode (SHE).

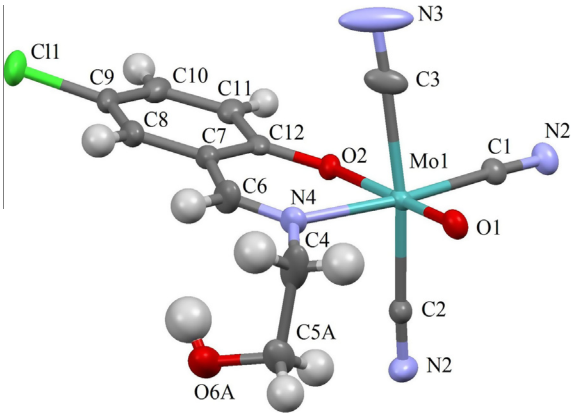


Fig. 1. Structure of the $[Mo(CN)_3O(clsb)]^{2-}$ ion in **2a** with the atom labelling scheme and 50% displacement ellipsoids.

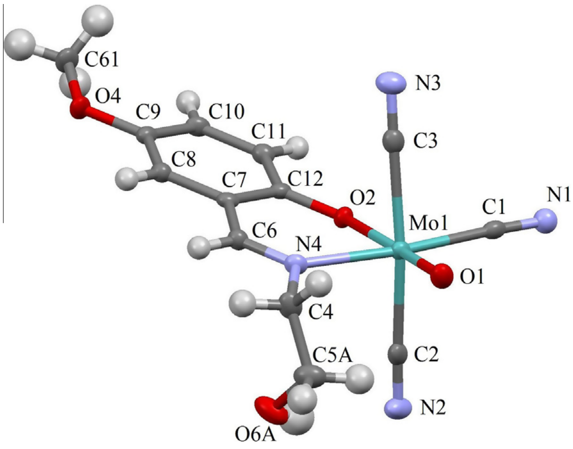


Fig. 2. Structure of the $[Mo(CN)_3O(metsb)]^{2-}$ ion in **3** with the atom labelling scheme and 50% displacement ellipsoids.

2.2. Theoretical calculations

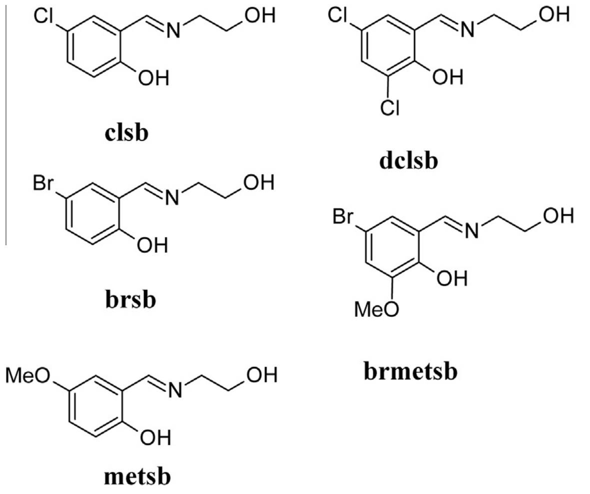
Quantum chemical calculations were performed using Turbomole 5.9 [23] and GAUSSIAN 09 [24] packages. The structures of the isolated $[Mo(CN)_3O(LL)]^{2-}$ anions (without counterions) were optimized in Turbomole at the DFT:B3LYP/def2-TZVP level, both in the gas phase and in a conductor-like screening model (COSMO) with $\varepsilon = 4$. In the case of **3**, the torsion angle C4–C5–O3–H3A (see Fig 2) was constrained to its value found in the crystal structure in order to prevent spurious rotation of the C–CH_2OH group leading to the formation of intramolecular hydrogen bonding with one of the CN ligands (which is not present in the crystal structure and thus should be considered as an artifact of the present simple model, not accounting for the environment of the $[M(CN)_3O(LL)]^{2-}$ anions). Mulliken and Hirshfeld atomic charges on the phenolic O atom of each LL ligand were obtained from single-point DFT:B3LYP/6-31G(d) calculations with GAUSSIAN 09, performed for the isolated LL^- fragments at their geometries cut from the previously optimized $[Mo(CN)_3O(LL)]^{2-}$ structures.

2.3. Synthesis

The ligands used in the synthesis are presented in Scheme 1. They were synthesized *in situ* by the reaction of the appropriate substituted salicylaldehyde and aminoethanol. The formed Schiff bases were denoted as Hclsb, Hbrsb, Hmetsb, Hdclsb and Hbrmetsb for 5-chloro-, 5-bromo-, 5-methoxy-, 3,5-dichloro- and 5-bromo-3-methoxy-salicylaldehyde, respectively.

2.3.1. Synthesis of $[PPh_4]_2[Mo(CN)_3O(brsb)]\cdot 3H_2O$ (**1**)

2-Aminoethanol (39 μl, 0.650 mmol) and 5-bromosalicylaldehyde (130.6 mg, 0.650 mmol) in 15 cm^3 ethanol were refluxed for 10 min. The solution was cooled to room temperature and a solution of $K_3Na[Mo(CN)_4O_2]\cdot 6H_2O$ (378.8 mg, 0.788 mmol) in 25 cm^3 water was added. The reflux was continued for 20 min. Thereafter tetraphenylphosphonium chloride (750.0 mg, 2.00 mmol) was added and the solution was left for crystallization. After a few hours sparkling dark green crystals were obtained. The compound was filtered, washed with water and dried in air. Yield 673.6 mg, 87%. MW 1165.89. *Anal.* Calc. for $C_{60}H_{55}BrMoN_4O_6P_2$: C, 61.81; H, 4.75; N 4.81. Found: C, 62.16; H, 4.565; N, 4.96%.



Scheme 1.