

## The first molybdenum dioxo compounds with $\eta^2$ -pyrazolate ligands: crystal structure and oxo transfer properties

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**Molybdenum dioxo compounds [MoO<sub>2</sub>Cl( $\eta^2$ -pz)] and [MoO<sub>2</sub>( $\eta^2$ -pz)<sub>2</sub>] with pz =  $\eta^2$ -3,5-di-*tert*-butylpyrazolate have been synthesized; crystallographic data, catalytic activity, and oxo transfer properties are described.**

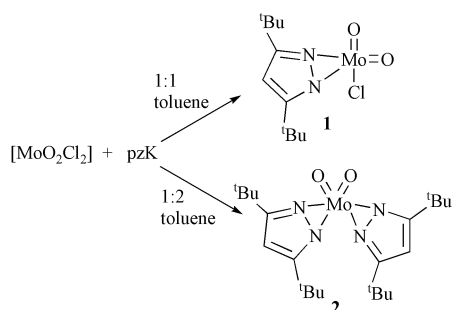
Molybdenum(vi) complexes containing the *cis*-[MoO<sub>2</sub>]<sup>2+</sup> core have been extensively studied in recent years due to their applications in biological and industrial oxidation processes and oxo-transfer reactions.<sup>1</sup> Research has been focussed on the variation of the co-ligands ([LL'/MoO<sub>2</sub>]) LL' to influence steric as well as redox properties.<sup>2,3</sup> In particular, O,S-based systems have received considerable attention, due to the assumption that these atoms are essential in the coordination sphere of molybdenum-containing enzymes.<sup>1,4</sup> In addition, tris(pyrazolyl)borate N-donor ligands have rendered a significant impact in this field producing a variety of Mo(IV), Mo(V) and Mo(VI) complexes.<sup>5–7</sup> The role of these tripodal ligands as functional models for various facets of enzyme structures and reactivity is believed to arise from their capability to block one face of the metal site and control the reactivity of the other.<sup>6,8</sup> On the other hand, development of mononuclear complexes with unlinked pyrazolate ligands is often hampered by their preference to build up bridging structures.<sup>9</sup> Recently, mononuclear pyrazolate complexes have been prepared by the introduction of sterically demanding groups in 3- and 5-positions featuring unusual  $\eta^2$ -coordination of the heterocycle.<sup>10</sup> Whereas most of the reported examples contain d<sup>0</sup> metal centers giving stable complexes according to HSAB reasons, we have shown recently that moderately reduced centers retain the  $\eta^2$ -coordination.<sup>11</sup> This prompted us to investigate sterically demanding pyrazolates as spectator ligands for molybdenum centers in high oxidation states. Herein we describe the first [MoO<sub>2</sub>]<sup>2+</sup> complexes stabilized by <sup>t</sup>Bu substituted pyrazolates and their catalytic oxo-transfer reactivity.

Treatment of [MoO<sub>2</sub>Cl<sub>2</sub>] with one or two equivalents of potassium 3,5-di-*tert*-butylpyrazolate (pzK) in toluene at room temperature afforded [MoO<sub>2</sub>Cl( $\eta^2$ -pz)] (**1**) and [MoO<sub>2</sub>( $\eta^2$ -pz)<sub>2</sub>] (**2**) in good yields, respectively (Scheme 1). Both compounds can be purified by sublimation at 120–130 °C under reduced pressure to give pale yellow **1** and colorless **2** pointing to a thermal stability of these systems. The crystalline complexes are readily soluble in common organic solvents such as toluene, THF and pentane. They are stable in dry air, whereas moisture

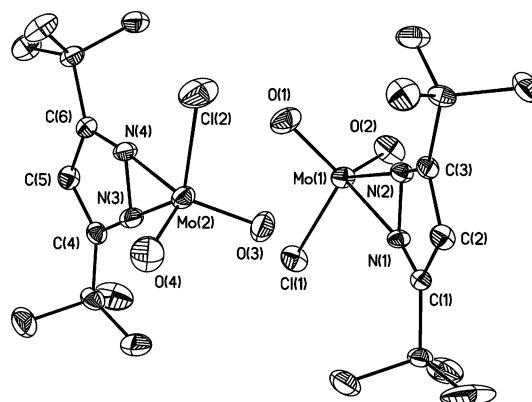
leads to immediate decomposition forming blue intractable solids. Single crystals suitable for X-ray diffraction analysis of **1** were obtained by recrystallization from concentrated toluene solutions,<sup>†</sup> whereas several attempts to solve the structure of **2** were unsuccessful due to twinning problems.

The <sup>1</sup>H NMR spectra in toluene-*d*<sub>6</sub> between +20 and –80 °C show for both compounds one set of resonances each for symmetrically coordinated ligands ( $\delta$  1.12; 6.09 ppm for **1** and 1.20; 6.29 ppm for **2**) implying dynamic processes in solution. However, if the structural arrangement of **2** were trigonal prismatic with the molybdenum and the two oxygen atoms residing in a mirror plane, the <sup>t</sup>Bu groups would become magnetically equivalent. Interestingly, this situation would be approaching the structure found in DMSO-reductases, where the crystal structure analysis shows a trigonal prism with Mo=O approximately being *trans* to one of the ligands.<sup>12</sup> <sup>95</sup>Mo NMR spectroscopy reveals for **1** a resonance at  $\delta$  37.3 ppm, whereas that for **2** is shifted to higher field ( $\delta$  –147.2 ppm) consistent with an increased electron density at the metal center. By mass spectrometry, the [M<sup>+</sup>] species with correct isotope pattern are observed. The IR spectra display two strong  $\nu_{\text{Mo=O}}$  bands at 971 and 941 cm<sup>–1</sup> for **1**, and for **2** at 951 and 922 cm<sup>–1</sup>, characteristic for symmetric and asymmetric vibrational modes, respectively, of the *cis*-[MoO<sub>2</sub>]<sup>2+</sup> fragment.<sup>4</sup> Determination of the molecular mass by vapor pressure osmometry in toluene shows **1** and **2** to be monomeric in solution.

Fig. 1 shows the molecular structure of [MoO<sub>2</sub>Cl( $\eta^2$ -pz)] (**1**) along with selected bond lengths and angles. The asymmetric unit contains two independent molecules. Both exhibit square pyramidal geometries around the molybdenum atom with one of the oxygen atoms residing in the apical position. The dihedral angle between the Mo–N–N plane and the N–C–C–N best plane is 4.4° for Mo(1) and 16.2° for Mo(2). The molybdenum–nitrogen bond lengths are 2.038(3), 2.106(3), 2.090(3) and 2.035(3) Å, consistent with  $\eta^2$ -coordination. The molybdenum–



Scheme 1

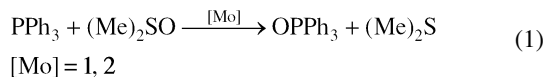


**Fig. 1** Molecular structure of [MoO<sub>2</sub>Cl( $\eta^2$ -pz)] (**1**). Selected bond lengths (Å) and angles (°): Mo(1)–O(1) 1.698(2), Mo(1)–O(2) 1.684(3), Mo(1)–N(1) 2.106(3), Mo(1)–N(2) 2.038(2), Mo(1)–Cl(1) 2.310(3), Mo(2)–O(3) 1.694(3), Mo(2)–O(4) 1.681(3), Mo(2)–N(3) 2.035(3), Mo(2)–N(4) 2.090(3), Mo(2)–Cl(2) 2.291(3); C(1)–N(1)–Mo(1) 163.3(2), C(3)–N(2)–Mo(1) 164.3(2), C(4)–N(3)–Mo(2) 175.2(2), C(6)–N(4)–Mo(2) 175.1(2).

oxygen and molybdenum–chlorine bond lengths are similar to related ones described in the literature.<sup>5,13</sup> A relatively short intermolecular distance between Mo(1) and O(3) of 2.763 Å is noticeable, but the assumption of a bonding interaction does not seem to be justified due to a normal Mo(2)=O(3) bond length of 1.694(3) Å, which is comparable to the other M=O bond lengths of 1.681(3), 1.698(2) and 1.684(3) Å.

Oxo transfer reactions of complexes **1** and **2** to one equivalent of PPh<sub>3</sub> were investigated. <sup>31</sup>P NMR spectra of the experiment performed with compound **2** and PPh<sub>3</sub> in toluene-*d*<sub>8</sub> at 80 °C were measured every 15 min. The signal for OPPh<sub>3</sub> increased gradually accompanied by an immediate broadening of the two signals (for PPh<sub>3</sub> and OPPh<sub>3</sub>) indicating the formation of a paramagnetic species. In addition, a color change from pale yellow to dark brown was observed. For ligand field reasons monomeric compounds of the type [LL'Mo<sup>IV</sup>O] are diamagnetic.<sup>14</sup> Dimeric [LL'(O)Mo<sup>V</sup>–O–Mo<sup>V</sup>(O)LL'] species, common in other systems,<sup>6,15</sup> are usually also described to be diamagnetic, however paramagnetism is possible in certain structural situations.<sup>16</sup> Therefore, the paramagnetism and the color indicate the formation of a Mo(v) species of the type [(η<sup>2</sup>-pz)<sub>2</sub>(O)Mo<sup>V</sup>–O–Mo<sup>V</sup>(O)(η<sup>2</sup>-pz)<sub>2</sub>], similar to [(acac)<sub>2</sub>(O)Mo<sup>V</sup>–O–Mo<sup>V</sup>(O)(acac)<sub>2</sub>], which is described as paramagnetic and dark brown.<sup>17</sup> The reaction of **1** with one equivalent of PPh<sub>3</sub> in toluene-*d*<sub>8</sub> at 80 °C leads also to the oxidation of PPh<sub>3</sub>. However, the <sup>31</sup>P NMR spectrum shows next to the signal for PPh<sub>3</sub> (δ –3.2) several signals including one at δ 43.9 ppm consistent with the formation of [MoOCl(η<sup>2</sup>-pz)(OPPh<sub>3</sub>)].<sup>18</sup> Presumably, the low coordination number at the metal site favors the phosphine oxide to coordinate.

Complexes **1** and **2** display catalytic activity for the oxidation of PPh<sub>3</sub> in the presence of DMSO, according to eqn. (1).



Typical experiments were performed in deoxygenated DMSO-*d*<sub>6</sub> solutions containing 4 × 10<sup>–3</sup> mol PPh<sub>3</sub> and 4 × 10<sup>–4</sup> mol catalyst and were monitored by <sup>31</sup>P NMR spectroscopy. Catalyst **1** oxidized 100% of PPh<sub>3</sub> within 2 h at rt, whereas with **2** the reaction temperature had to be raised at 80 °C. No reaction occurs between PPh<sub>3</sub> and DMSO without catalyst under these conditions. In both cases, the color of the reaction mixture remained slightly yellow in contrast to the stoichiometric reactions, indicating the equilibrium on the side of the dioxo molybdenum species. <sup>1</sup>H NMR spectra after complete conversion show signals for triphenylphosphine oxide and the intact catalysts. The formation of dimethyl sulfide was confirmed by gas chromatography. The use of DMSO as oxo donor in this study has biological relevance to the molybdenum-containing DMSO-reductases, which are able to utilize a variety of dialkyl- and alkylaryl sulfoxides as oxidizing substrates.<sup>2</sup>

The crystal structure of **1** provides the first structural evidence of a η<sup>2</sup>-coordinated pyrazolate ligand at a [MoO<sub>2</sub>]<sup>2+</sup> core. The low coordination number is interesting as five-coordinated dioxomolybdenum(vi) complexes are normally stabilized by additional donor molecules, by polymerization, or by bulky ligands<sup>19</sup> implying that the unique electronic features of the η<sup>2</sup>-bonded ligand are responsible and suggesting that other high-oxidation state metal complexes not accessible with other ligands may be stabilized with this systems. The compounds herein described facilitate oxo transfer to an acceptor substrate, the initial step for catalytic activity. In the presence of an oxygen donor, complexes **1** and **2** are efficient catalysts for this transfer reaction. The catalytic cycle demonstrates that the ligands are capable of stabilizing this system in

the presence of partially filled d-orbitals. Substitution of the chloride atom in **1** may allow a fine-tuning of the reactivity properties. Research in this field is in progress.

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## Notes and references

† Crystal data for **1**: C<sub>11</sub>H<sub>19</sub>ClMoN<sub>2</sub>O<sub>2</sub>, *M* = 342.67, monoclinic, space group *Cc*, *a* = 15.35(1), *b* = 10.28(1), *c* = 19.75(2) Å, β = 106.87(7)°, *V* = 2980(6) Å<sup>3</sup>, *T* = 133(2) K, *Z* = 8, μ(Mo–Kα) = 1.052 mm<sup>–1</sup>, *F*(000) = 1392. Data were collected in the range 2.61–27.91° (θ-scan), 5532 independent reflections (*R*<sub>int</sub> = 0.0363), final *R*<sub>1</sub> = 0.0217, with allowance for the thermal anisotropy of all non-hydrogen atoms. CCDC reference number 180085. See <http://www.rsc.org/suppdata/cc/b2/b205420e/> for crystallographic data in CIF or other electronic format.

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