SHORT PAPER

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Group 6 metal carbonyl complexes containing the 3,5-dimethyl-1,2,4-triazole ligand[†]

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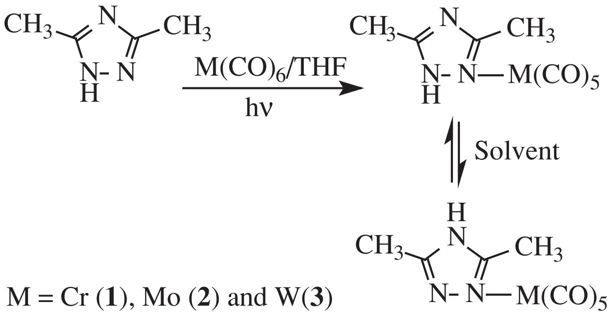
Three complexes, [M(CO)$_5$Tz], have been synthesised by the photochemical reaction of 3,5-dimethyl-1,2,4-triazole (Tz) with [M(CO)$_6$] (M = Cr, Mo and W). The crystal structure of [Cr(CO)$_5$Tz] has been characterised by X-ray analysis, and the 4*H*-tautomer of the triazole ligand is observed in this complex in the solid state.

Keywords: 3,5-dimethyl-1,2,4-triazole, group 6 carbonyl complexes

The coordination chemistry of 1,2,4-triazole ligands has been widely studied.[1] These ligands have variability in binding modes owing to the increased number of nitrogen atoms and the attendant possibilities for isomerism, compared with analogous pyrazole ligands.[2] A number of transition metals complexes containing 1,2,4-triazole ligands have been synthesised and characterised, which usually aggregate dinuclear, oligonuclear and polynuclear metal complexes.[1] However, only a few papers have described the coordination chemistry of 1,2,4-triazole ligands with group 6 metal carbonyl complexes.[3-11] Moreover, these group 6 metal carbonyl complexes with 1,2,4-triazole ligands usually are mononuclear; and 1,2,4-triazole ligands also exhibit η^1-bonding to a single metal.

We are interested in the synthesis of group 6 metal carbonyl complexes of N-containing aromatic heterocyclic ligands with N–H bonds. Our recent investigation shows that such complexes have interesting structural features, which can be linked into a one-dimensional chain structure via intermolecular hydrogen bonds interactions between the N–H groups and the oxygen atoms of metal carbonyls.[12] Now we continue our investigation of group 6 metal carbonyl complexes containing aromatic heterocyclic ligands. Herein we report the synthesis and structural characterisation of group 6 metal carbonyl complexes containing the 3, 5-dimethyl-1,2,4-triazole ligand.

The photochemical reactions of 3,5-dimethyl-1,2,4-triazole with [M(CO)$_6$] (M = Cr, Mo and W) in the molar ratio 1 : 1 at room temperature yield the title complexes (Scheme 1). All complexes are stable in the solid at low temperature, in solution the tungsten complex can also be handled in air, but the chromium and molybdenum complexes are slightly air-sensitive in solution. These complexes are soluble in polar solvents such as acetone and chlorinated solvents. The IR spectra of the complexes in the solid state show one broad characteristic absorption peak of the N-H stretching band at *ca* 3430 cm^{-1}. Five to six ν_{CO} bands are observed in all complexes probably due to a superposition of the absorption of two conformational isomers in the solid (Fig.1), which is similar to spectra of [M(CO)$_5$L] (M = Cr or W; L = ferrocenylpyrazole).[12] The ^{1}H NMR spectra of the three complexes discribed here exhibit the expected proton signals, but two sets of proton signals for the 3,5-dimethyl-1,2,4-triazole ligand are observed, which implies the existence of two isomers in solution. The ^{1}H NMR spectrum of [Cr(CO)$_5$Tz] at higher temperature still displays the mixture of two isomers, and the relative amount of isomers does not significantly change. The existence of two isomers may be attributed to the NH-tautomeric equilibrium[1] in solution as shown in Scheme 1, which cannot give a time-averaging signal on the NMR time scale. In fact, the crystal structure of [Cr(CO)$_5$Tz] in the solid state shows that the NH-tautomeric equilibrium could exist in solution.



Scheme 1

In general, triazole ligands coordinate to metals by the *N*1 atom, and the tautomer is exclusively the 1*H*-tautomer in the solid; few 4*H*-tautomers are reported in the literature.[1] However, as shown in Fig.1, a stable 4*H*-tautomer of the triazole ligand is observed in complex [Cr(CO)$_5$Tz] in the solid state, which may arise from the tautomeric equilibrium (Scheme 1) and is stabilised by the coordination to the metal.[1] This structure also consists of two crystallographically independent molecules (**A** and **B**). The two molecules are essentially the same. The main differences between them are the angles, such as ∠C(3)–Cr(1)–N(1) (179.6(2)°) and ∠C(2)–Cr(1)–C(5) (177.4(3)°) in **A** while ∠C(12)–Cr(2)–N(4) (176.4(2)°) and ∠C(13)–Cr(2)–C(10) (171.1(2)°) in **B**, respectively, which may be the results of the repulsion of the methyl groups with the carbonyls. The Cr–N distances in the two molecules (2.132(4) Å in **A** and 2.129(4) Å in **B**) are analogous, which is similar with that observed in [Cr(CO)$_5$(3,4,5Me$_3$Pz)] (2.137(3) Å, Pz = pyrazole),[13] but longer than that in [Cr(CO)$_5$(4MeTrz)] (2.111(2) Å, Trz = 1,2,4-trizazole).[9] It is also noteworthy that the Cr–C distances *trans* to the triazole ligand in **A** and **B** are 1.810(5) Å and 1.838(6) Å, respectively, and shorter than the other four *cis* Cr–C distances in the two molecules, while the corresponding C–O distance is longer than other four C–O distances, respectively. In addition, the two molecules are linked into a

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

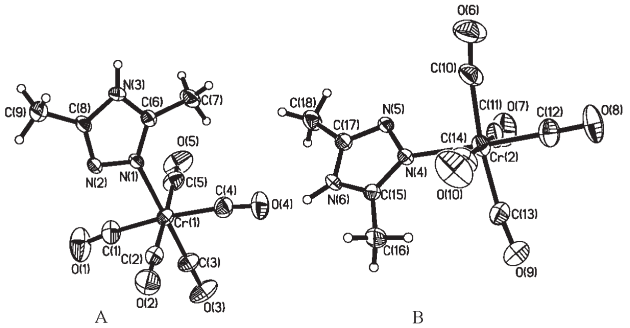

Fig. 1 The molecular structure of $Cr(CO)_5Tz$. Selected bond distance [Å] and angles [°]: Cr(1)—N(1) 2.132(4), Cr(1)—C(1) 1.870(6), Cr(1)—C(3) 1.810(5), O(3)—C(3) 1.173(5), O(2)—C(2) 1.147(5), Cr(2)—N(4) 2.129(4), Cr(2)—C(11) 1.901(6), Cr(2)—C(12) 1.838(6), O(8)—C(12) 1.155(6), O(7)—C(11) 1.136(6), N(3)—H...N(5)[a] 2.870 and N(6)—H...N(2)[b] 2.871; C(3)—Cr(1)—N(1) 179.6(2), C(2)—Cr(1)—C(5) 177.4(3), C(12)—Cr(2)—N(4) 176.4(2), C(13)—Cr(2)—C(10) 171.1(2), N(3)—H...N(5)[a] 156.55 and N(6)—H...N(2)[b] 166.86 (symmetry code: $a = -x, -y + 1, -z + 1$; $b = -x + 1, -y + 1, -z + 1$).

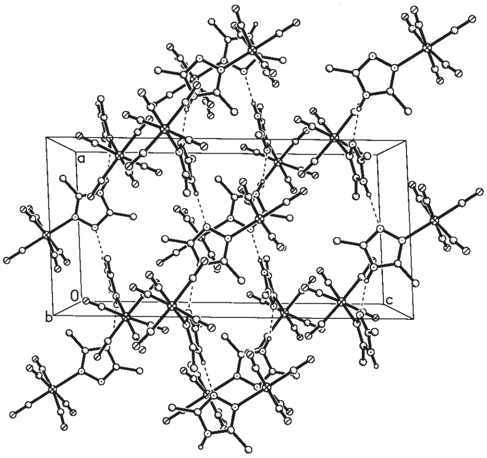

Fig.2 The crystal packing diagram of $Cr(CO)_5Tz$ emphasising the hydrogen bonding interactions.

one-dimensional chain via the intermolecular N—H..N hydrogen bonds interactions (Fig. 2). The hydrogen bond N—H…N distances are 2.870 and 2.871 Å, respectively.

Experimental

Reaction of 3,5-dimethyl-1,2,4-triazole (Tz) with $M(CO)_6$ (M = Cr, Mo and W): a solution of $M(CO)_6$ (1 mmol) and 3,5-dimethyl-1,2,4-triazole (1 mmol) dissolved in THF (20 ml) was irradiated with a 300 W high-pressure mercury lamp for *ca* 14 h at room temperature. After the reaction was complete, the solvent was removed *in vacuo* and the residual solid was purified by column chromatography on silica, using ethyl acetate/hexane as eluent. The yellow eluent was concentrated to dryness under reduced pressure. The residual solid was recrystallised from CH_2Cl_2/hexane to give a yellow crystalline solid.

Data for $Cr(CO)_5Tz$: Yield: 78%. ^1H NMR ($CDCl_3$): (25°C) δ 2.41, 2.47, 2.58 (s, s, s, CH_3), 9.26, 10.03 (s, s, NH, *ca.* 40 : 60); (35°C) 2.40, 2.47, 2.58 (s, s, s, CH_3), 9.19, 10.10 (s, s, NH, *ca* 42 : 58); (45°C) 2.40, 2.46, 2.57 (s, s, s, CH_3), 9.22, 10.12 (s, s, NH, *ca* 41 : 59). IR (KBr): ν_{CO} 1870.0 (s), 1907.4 (vs), 1929.7 (sh), 1953.7 (sh), 1976.4(sh), 2066.0 (m) cm^{-1}; ν_{NH} 3431.6 (br, m) cm^{-1}. Found: C, 37.10; H, 2.17; N, 14.21%. $C_9H_7CrN_3O_5$ requires C, 37.37; H, 2.42; N, 14.53%.

Data for $Mo(CO)_5Tz$: Yield: 73%. ^1H NMR ($CDCl_3$, 25°C): δ 2.43, 2.49, 2.59 (s, s, s, CH_3), 9.43, 10.41 (s, s, NH, *ca* 47 : 53). IR (KBr): ν_{CO} 1880.4 (s), 1909.2 (vs), 1928.7 (sh), 1958.4 (sh), 1981.4(sh), 2072.4 (m) cm^{-1}; ν_{NH} 3429.8 (br, m) cm^{-1}. Found: C, 32.50; H, 2.18; N, 12.72%. $C_9H_7MoN_3O_5$ requires C, 32.43; H, 2.10; N, 12.61%.

Data for $W(CO)_5Tz$: Yield: 81%. ^1H NMR ($CDCl_3$, 25°C): δ 2.47, 2.59 (s, s, CH_3, *ca* 21), 2.63, 2.77 (s, s, CH_3, *ca* 79), The proton of NH was not found. IR (KBr): ν_{CO} 1878.4 (sh), 1902.7 (vs), 1921.7 (vs), 1971.0 (m), 2070.5 (m) cm^{-1}; ν_{NH} 3427.2 (br, w) cm^{-1}. Found: C, 25.52; H, 2.13; N, 9.55%. $C_9H_7N_3O_5W$ requires C, 25.71; H, 1.67; N, 10.00%.

Crystal data for $Cr(CO)_5Tz$: $C_9H_7CrN_3O_5$, M = 289.18, monoclinic space group P2(1)/c, a = 9.583(3), b = 13.995(4), c = 19.429(5) Å, β = 92.831(5)°, V = 2602.4(12) Å^3, Z = 8, ρ_{calc} = 1.476 Mg m^{-3}, μ(MoKα) = 0.894 mm^{-1}, T = 293(2) K. 10547 Reflections of which 4603 with $I > 2\sigma(I)$ were measured ($1.79 < \theta < 25.03°$) on a Siemens SMART/CCD area detector equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was resolved by the direct method and refined by full-matrix least-squares on F^2 using the SHELXL-97 program, R_1 = 0.0491 and R_w = 0.0855 with GOF = 0.898. Full crystallographic details have been deposited at the Cambridge Crystallographic Data Centre (CCDC 202435).

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