The Crystal and Molecular Structure of [(μ-4,4′-Dimethyl-2,2′-bipyridyl)bis(pentacarbonylchromium(0))]: The First Structural Determination of a Complex Containing a Bridging 2,2′-Bipyridyl Ligand

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Species of the type $M(CO)_5(bipy)$, containing monodentate 2,2′-bipyridyl (bipy) ligands, have been detected as intermediates following the photolysis of $M(CO)_6$ (M = Cr, Mo, or W) in the presence of excess bipy [1–3]. These intermediates have not been isolated and the mechanism of the following chelation step, to yield $M(CO)_4(bipy)$, is not clear; the excess of ligand used to promote the formation of the monodentate species may influence the kinetics of the chelation step.

Recently, the stable monodentate complexes $M(CO)_5(dpm)$ [4] and $M(CO)_5(dipyam)$ [5] (M = Cr or Mo; dpm = di-2-pyridylmethane, $(C_5H_5N)_2CH_2$; dipyam = di-2-pyridylamine, $(C_5H_5N)_2NH$) have been isolated from the reactions of dpm or dipyam with the photochemically generated $M(CO)_5(thf)$. These complexes are converted on gentle warming to the corresponding chelate species, with the liberation of $M(CO)_6$ and free ligand, eqn. (1):

$$2M(CO)_5L \xrightarrow{\Delta} M(CO)_4L + M(CO)_6 + L \qquad (1)$$

Clearly this reaction must involve a dissociative step.

These observations led us to investigate further the formation of non-chelate bipyridyl complexes and we have now obtained [(μ-(4,4′-dimethyl-2,2′-bipyridyl)bis(pentacarbonylchromium(0))], $[Cr(CO)_5]_2(dmbipy)$ (**1**), from the reaction of the solid (*cis*-cyclooctene)pentacarbonylchromium(0) [6] with dmbipy in pentane at room temperature. The compound was identified by elemental analysis and very small red–brown crystals, of marginal quality for X-ray work, were obtained from toluene solution at −30 °C. Toluene was the only solvent suitable for growing crystals as more polar solvents react with **1**, while **1** is not sufficiently soluble in the less polar alkane solvents. Also, compound **1** contains a chiral centre and many of the crystals grown from toluene appeared to be twinned. Efforts are currently underway to improve the quality of the single crystals.

An X-ray structure determination to $R = 0.10$ confirms the bipyridyl-bridged binuclear structure of the molecule (Fig. 1). This is the first fully authenticated example of a stable non-chelate 2,2′-bipyridyl complex. Principal bond lengths and angles are all within expected ranges [7], although the orientations of Cr(1)–N(1) and Cr(2)–N(12) relative to the ligand skeleton suggest a degree of crowding of the $Cr(CO)_5$ moieties. A striking and unexpected feature is the mutually perpendicular orientation of the ligand pyridyl rings (the experimentally determined angle is 89°). The UV–Vis data for **1** indicate that the pyridyl rings are not coplanar [8], and so we consider that this perpendicular arrangement represents the preferred molecular geometry and is not simply imposed by crystal-packing requirements.

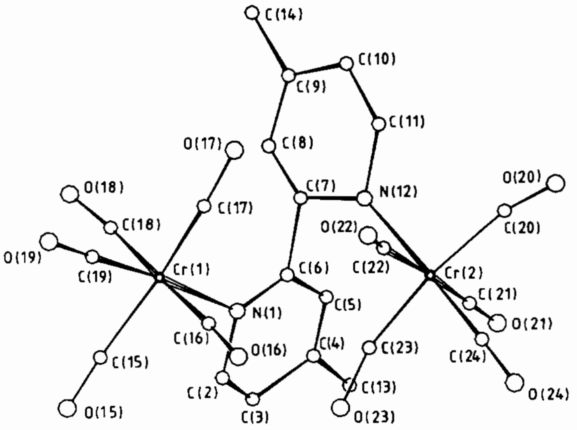

Fig. 1. Structure of [(μ-4,4′-dimethyl-2,2′-bipyridyl)bis(pentacarbonylchromium(0))].

The binuclear complex transforms on warming in solution to $Cr(CO)_4(dmbipy)$ and $Cr(CO)_6$ (eqn. (2)); the mechanism of this process will be discussed in a forthcoming paper [8]. Our observations raise the possibility that the binuclear species $[M(CO)_5]_2(bipy)$ may also be involved in the photoinduced reactions mentioned above.

$$[Cr(CO)_5]_2(dmbipy) \xrightarrow{\Delta} Cr(CO)_4(dmbipy) + Cr(CO)_6 \qquad (2)$$

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Experimental

Crystal Data for 1

$C_{22}H_{22}N_2O_{10}Cr_2$, $M = 568.4$; monoclinic, $P2_1$; $a = 9.321(20)$, $b = 12.361(13)$, $c = 10.564(2)$ Å; $\beta = 100.09(16)°$, $U = 1198$ Å^3, $Z = 2$, $D_c = 1.575$ g cm^{-3}; λ(Mo Kα) = 0.71069 Å, $\mu = 9.41$ cm^{-1}. Data were measured on a Nicolet P3 four-circle diffractometer, using an ω–2θ scan technique, to yield 939 observations with $I > 3\sigma(I)$. The positions of all non-hydrogen atoms were determined using SHELXS86. Structure factors for neutral atoms were taken from ref. 9. After refinement R was 0.14, but after excluding about 120 weak reflections with $\Delta F/F > 0.4$ the values of R and R' fell to 0.10 and 0.13, respectively, for 155 refined parameters and 816 F values. The Cr atom was refined anisotropically; other atoms were treated isotropically and because of the limit and quality of the data no attempt was made to locate the H atoms nor to determine the absolute configuration of the molecule. The maximum feature in the final difference map was 0.8e Å^{-3} and the distribution of ΔF against $|F_o|$ and $(\sin 2\theta)^2$ was satisfactory. Thus, although the structure is determined with no great accuracy, there is no reason to assume that it is in any way incorrect.

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