

GROUP VIB CARBONYL COMPLEXES OF PYRAZINO[2.3-*f*]QUINOXALINE OR 1,4,5,8-TETRAAZAPHENANTHRENE (TAP)

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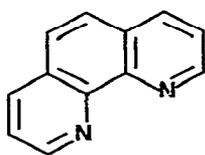
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Summary

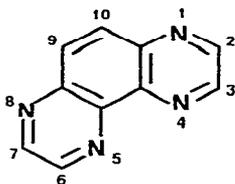
1,4,5,8-Tetraazaphenanthrenemetal tetracarbonyl complexes (metal = Cr, Mo, W) have been synthesized. The CO force constants show that there is more back-bonding in these complexes than in the analogous 1,10-phenanthroline complexes, because of the two additional electron-withdrawing nitrogen atoms. The $M \rightarrow L$ CT transitions show a strong bathochromic shift relative to the corresponding *o*-phenanthroline complexes.

Introduction

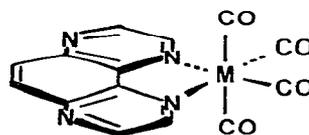
The properties of transition metal complexes frequently involve some contribution from back-bonding, and this metal-to-ligand π -electron donation depends on the electron-attracting ability of the ligands; we considered it would thus be of interest to look into this aspect of organometallic bonding by synthesising and examining the properties of a series of complexes similar to $M(\text{CO})_4(o\text{-phen})$ in which the *o*-phenanthroline (I) ligand would be replaced by pyrazino[2.3-*f*]quinoxaline or 1,4,5,8-tetraazaphenanthrene (II, hereafter abbreviated as TAP). This aza-analog of *o*-phenanthroline possesses two addi-



(I)



(II)



(III a, $M = \text{Cr}$;

III b, $M = \text{Mo}$;

III c, $M = \text{W}$)

tional electron-withdrawing nitrogen atoms, which should increase the strength of back-bonding by enhancing the π -deficiency of the heterocycle. The study envisaged was made possible by the recently improved synthesis of TAP and numerous derivatives [1,2].

We present below the synthesis of complexes of the general structure $M(\text{CO})_4\text{-TAP}$ (IIIa, IIIb, IIIc) and the infrared spectra in the $\nu(\text{CO})$ region, used as a probe for back-bonding [3].

Synthesis

The complexes were made photochemically by irradiating vacuum-degassed solutions of equimolar amounts of TAP and the corresponding metal hexacarbonyl, the flask being evacuated at regular intervals to remove the carbon monoxide. In spite of this, the yields are not quantitative, even after prolonged irradiation; increasing the photolysis time results in practically no change, the amounts of free ligand and complex remaining almost constant. This slowing down of the reaction is probably to be ascribed to an inner filter effect, the new complex absorbing most of the light (see Fig. 1).

A point of interest is the question of whether the reaction requires one or two photons. Three mechanisms may be envisaged to describe the replacement of two carbonyl groups by one chelating molecule: mechanisms 1 and 2 involve two photons per complex formed whereas pathway 3 only uses one photon. A choice between these possibilities can be made by taking advantage of the fact that irradiation of $\text{Cr}(\text{CO})_6$ in tetrahydrofuran (THF) has been shown by

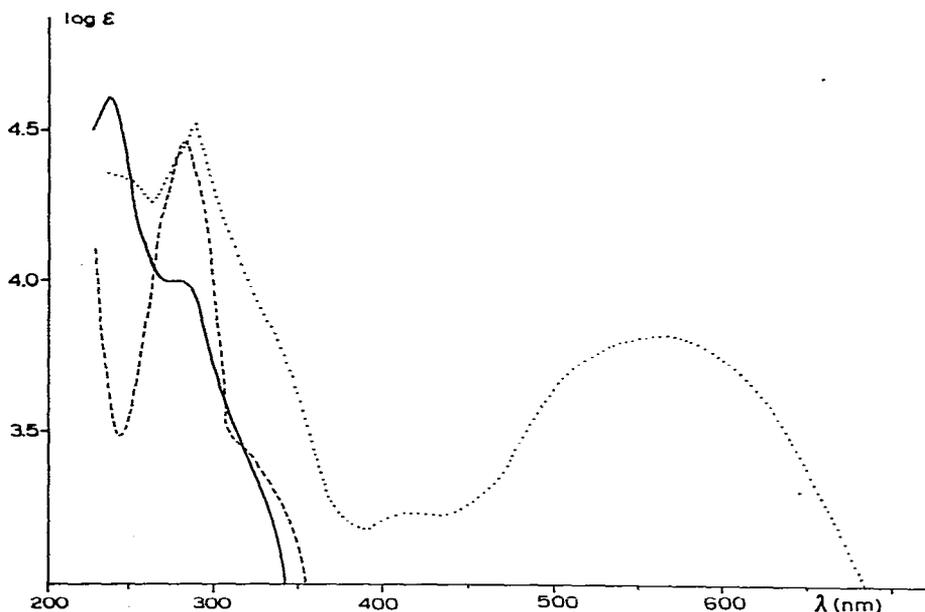
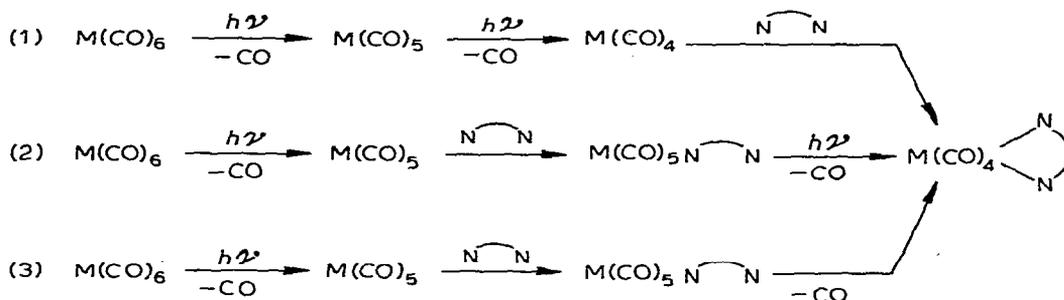
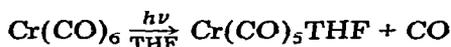


Fig. 1. UV spectra of $\text{Cr}(\text{CO})_6$ (—), TAP (-----), $\text{Cr}(\text{CO})_4\text{TAP}$ (.....) in methanol.



Strohmeier [4] to stop at monosubstitution:



and that the resulting pale yellow complex reacts with a variety of ligands to undergo a facile substitution of the THF molecule. We thus photolysed $\text{Cr}(\text{CO})_6$ in THF; a solution of TAP in the same solvent was then added in the dark and under vacuum. The mixture turned from yellow to reddish-brown and then to dark-blue in a few minutes, and gave a 70% yield (estimated by IR) of the chelate. We take this result as favouring mechanism 3.

Infrared spectra and back-bonding

The vibrational properties of carbonyl groups in transition metal complexes are often interpreted in terms of bonding between the metal and the other ligands. It is clear, however, that IR frequencies of such highly-coupled oscillator systems are not quantitatively indicative of bond properties, and that force constants have to be extracted from the spectra. Having four experimental frequencies allowed us to relieve one of the constraints included in the simplified Cotton-Kraihanzel force field [5,6]; we have thus assumed that the interaction force constant between the *trans* carbonyls is twice that between one axial and one equatorial CO, i.e. $k'_t = 2k''$, and that the interaction constant between the two *cis* carbonyls had a value different from both k'_t and k'' . The assignments given in Table 1 are supported by the observation that the band labelled "axial"

TABLE 1

CARBONYL STRETCHING FREQUENCIES (CHCl_3) AND CALCULATED FORCE CONSTANTS FOR $\text{M}(\text{CO})_4\text{L}$

Complex	$\nu(\text{CO})$ (cm^{-1})				$k_{\text{ax}}(\text{CO})$ ($\text{md } \text{Å}^{-1}$)	$k_{\text{eq}}(\text{CO})$ ($\text{md } \text{Å}^{-1}$)
	axial		equatorial			
$\text{Cr}(\text{CO})_4(o\text{-phen})$	2008	1907	1883	1831 [7]	15.39	14.09
$\text{Cr}(\text{CO})_4\text{TAP}$	2010	1920	1905	1855	15.51	14.43
$\text{Mo}(\text{CO})_4(o\text{-phen})$	2014	1910	1881	1833 [7]	15.46	14.09
$\text{Mo}(\text{CO})_4\text{TAP}$	2020	1925	1905	1855	15.63	14.43
$\text{W}(\text{CO})_4(o\text{-phen})$	2010	1901	1877	1831 [7]	15.34	14.05
$\text{W}(\text{CO})_4\text{TAP}$	2010	1925	1895	1850	15.47	14.32

TABLE 2
M → L CT TRANSITIONS OF M(CO)₄L IN METHANOL

Metal	o-phen		TAP	
	λ _{max} (nm)	log ε	λ _{max} (nm)	log ε
Cr	491	3.7	568	3.5
Mo	461	3.8	527	3.7
W	476	3.9	548	3.8

at higher wavenumber is weak and fine, as it should be if the two "axial" carbonyls are almost colinear.

It is clearly seen that the two additional nitrogen atoms increase the force constants for both "axial" and "equatorial" carbonyls; according to the usual interpretation, this is diagnostic for weaker M—CO bonding, and consequently to stronger M—L back-bonding, in agreement with the assumption we made in the introduction.

The enhanced back-bonding in these new complexes awaits confirmation from chemical and kinetic studies. We have, however, already found that a methanol solution (10⁻⁵ mol l⁻¹) of Cr(CO)₄TAP is much more resistant to atmospheric degradation than an identical Cr(CO)₄(o-phen) solution. When followed by UV-vis absorption spectrometry, the loss of TAP complex is less than 20% in 2.5 h, whereas the phenanthroline complex absorption fades away with a half-life of approximately 1 h.

Electronic spectra

Back-donation of metal *d* electrons to ligands is enhanced when the LUMO (lowest unoccupied molecular orbital) energy is lowered; in the case of *o*-phenanthrolines, this can be achieved by introducing electron-attracting groups into the organic molecules [8]. The two additional nuclear nitrogen atoms of TAP should bring about a similar energy change, and must be reflected in the M → L CT (metal-to-ligand charge transfer) transitions.

The visible absorption in the 460–500 nm region observed for M(CO)₄(*o*-phen) complexes (M = Cr, Mo, W) has been assigned [9] to M → L CT absorption; one would thus expect this transition to undergo a bathochromic shift when *o*-phenanthroline (I) is replaced by TAP (II). Table 2 lists the relevant data, which support the above reasoning.

Experimental

The IR spectra in the CO stretching region were recorded on a Perkin—Elmer 357 spectrometer. UV-Visible electronic absorption spectra were measured with a Unicam SP 1800 spectrophotometer. Metal hexacarbonyls (Strem Chemicals) were sublimed before use (25°C/10⁻³ Torr).

The M(CO)₄TAP complexes (IIIa—IIIc) were synthesised by irradiation, with stirring, at 25°C of the corresponding M(CO)₆ (10⁻³ mol) in the presence of

TAP (10^{-3} mol) in anhydrous benzene or THF (40–50 ml). Photolyses (6 h) were performed in a Pyrex flask with two Philips HPK 125 W medium pressure mercury arc. Degassing of the solutions before irradiation was achieved by four successive freezing, pumping and thawing cycles at 10^{-4} Torr and additional ones during the photolysis to remove the carbon monoxide. The deep violet reaction mixture was concentrated by rotary evaporation (25°C). The dark residue was adsorbed on microcrystalline cellulose and chromatographed on silica gel (0.063–0.02 mm). $\text{M}(\text{CO})_4\text{TAP}$ were eluted with ethyl acetate and unchanged ligand desorbed with acetone. Analytical samples were obtained after dissolution in the minimal amount of dichloromethane, precipitation with excess of n-hexane and the mixture kept at -20°C for a few hours. Crystals of the tetracarbonyl complexes III are reasonably stable at room temperature but decompose on heating.

IIIa (69%), found: C, 48.3; H, 1.8; N, 16.2. $\text{C}_{14}\text{H}_6\text{CrN}_4\text{O}_4$ (mol. wt 346.2) calcd.: C, 48.6; H, 1.8; N, 16.3%. UV (CH_3OH) 284 nm ($\log \epsilon$ 4.3), 568 ($\log \epsilon$ 3.5).

IIIb (85%), found: C, 43.4; H, 1.5; N, 13.9. $\text{C}_{14}\text{H}_6\text{MoN}_4\text{O}_4$ (mol. wt 390.1) calcd.: C, 43.1; H, 1.5; N, 14.4%. UV (CH_3OH) 258 nm ($\log \epsilon$ 4.3), 284 ($\log \epsilon$ 4.4), 527 ($\log \epsilon$ 3.7).

IIIc (57%), found: C, 35.4; H, 1.3; N, 11.9. $\text{C}_{14}\text{H}_6\text{N}_4\text{O}_4\text{W}$ (mol. wt 478.1) calcd.: C, 35.2; H, 1.3; N, 11.7%. UV (CH_3OH) 252 nm ($\log \epsilon$ 4.5), 284 ($\log \epsilon$ 4.4), 548 ($\log \epsilon$ 3.8).

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