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^{13}C NMR SPECTRA OF CHROMIUM TETRACARBONYL COMPLEXES OF 1,4,5,8-TETRAAZAPHENANTHRENE AND 1,4,5,8,9,12-HEXAAZATRIPHENYLENE

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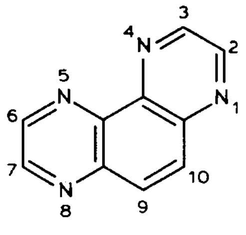
Summary

The ^{13}C NMR spectra of the chromium tetracarbonyl complexes $(TAP)Cr(CO)_4$ and $(HAT)Cr(CO)_4$ in both the carbonyl and the ligand region are assigned on the basis of substituent effects and $\{^1H\}$ single frequency ^{13}C spectra.

Following our previous investigations on the complexing properties of 1,4,5,8-te-



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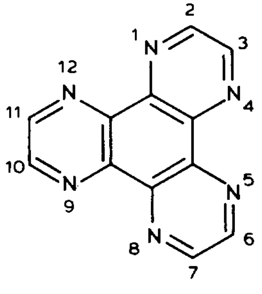

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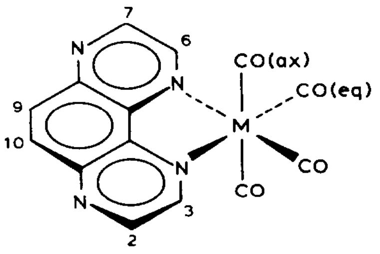

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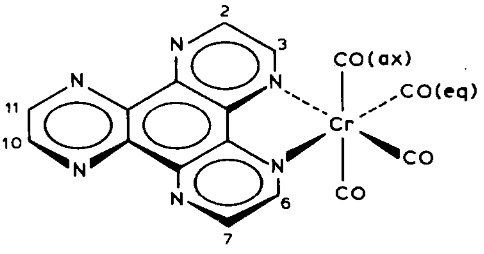

(IV)

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traazaphenanthrene (hereafter abbreviated as TAP, I) and 1,4,5,8,9,12-hexaazatriphenylene (HAT, II) and the bonding in the corresponding chromium tetracarbonyl complexes III and IV, we now report on the ^{13}C NMR spectra of these complexes, whose synthesis have been described, together with a discussion of their ^{1}H NMR and IR spectra [1,2,3].

1. Carbonyl ^{13}C shifts

The four carbonyl groups in III give two ^{13}C resonances with similar intensities and 18 ppm apart; the same is true for IV.

For III, the assignment of δ 230.3 ppm to the equatorial carbonyls rests on the observation that in the complexes bearing a TAP substituted in the 2- or 9-position, a separation of the lines appears at that δ value, corresponding to the carbonyl groups which become heterotopic, whereas the 212.4 ppm resonance remains unsplit, and must thus be related to the enantiotopic axial CO's. The assignment of the carbonyl shifts in IV is suggested by analogy. The corresponding data are listed in Table 1.

These assignments are in full agreement with those of Dobson and Asali [4] for (1,10-phenanthroline)chromium tetracarbonyl and opposite to those of Staal, Stufkens and Oskam [5] for (*N*,*N*′-di-t-butyl-1,4-diazabutadiene)chromium tetracarbonyl.

The enhanced back bonding observed on replacing *o*-phenanthroline by TAP previously showed up in the analysis of the stretching force constants derived from the IR spectrum in the carbonyl region [1–3]. The same effect is visible here, since the same modification leads to a 2.1 ppm downfield shift for the equatorial carbonyls, i.e. *trans* to the chelating ligand, whereas the signals for the carbonyls *cis* to the heterocyclic moiety are hardly affected. It is also clear that the major changes are caused by the additional nitrogen atoms *para* to the complexation site; an extra pyrazine ring (leading to HAT) or added substituents in the 2- or 9-positions cause no appreciable changes in the chemical shifts; the changes observed are too small to warrant discussion.

TABLE 1

CARBONYL ^{13}C CHEMICAL SHIFTS IN CHROMIUM CARBONYL COMPLEXES (Solvent $CDCl_3$; ppm downfield from internal TMS)

Complex	$\delta(CO_{eq})$	$\delta(CO_{ax})$
(bipy)$Cr(CO)_4$ [4]	227.2	212.7
(*o*-phen)$Cr(CO)_4$ [4]	228.2	212.8
(TAP)$Cr(CO)_4$	230.3	212.4
(2-Cl-TAP)$Cr(CO)_4$	230.0 and 230.8	212.5
(9-CH_3O-TAP)$Cr(CO)_4$	230.2 and 230.7	212.6
(9-$C_5H_{10}N$-TAP)$Cr(CO)_4$ [a]	230.2 and 230.5	212.9
(HAT)$Cr(CO)_4$	230.5	212.3
$Cr(CO)_6$ [6,7]	212.1	

[a] $C_5H_{10}N$ is 1′-piperidino.

TABLE 2

LIGAND ^{13}C CHEMICAL SHIFTS IN $(TAP)Cr(CO)_4$ AND $(HAT)Cr(CO)_4$ (Solvent $CDCl_3$; ppm downfield from internal TMS.)

$(TAP)Cr(CO)_4$	C(2,7)	C(3,6)	C(4a,4b)	C(8a,10a)	C(9,10)	
δ	146.2	147.3	141.8	144.7	132.2	
$\Delta\delta$ [a]	−0.3	+2.1	+0.8	+0.3	+0.3	
$^1J(^2J)$/Hz	186.8(9)	187.7(12)			168.8	
Δ^1J [a]/Hz	+4.0	+2.6			+1.4	
$(HAT)Cr(CO)_4$	C(2,7)	C(3,6)	C(4a,4b)	C(8a,12b)	C(8b,12a)	C(10,11)
δ	146.4	148.5	143.4	143.1 [b]	142.3 [b]	147.7
$\Delta\delta$ [a]	−0.7	+1.4	+1.1	+0.7	−0.1	+0.6

[a] Coordination shifts: $\Delta X = X((TAP)Cr(CO)_4) - X(TAP)$ [9] or $X((HAT)Cr(CO)_4) - X(HAT)$ [9]. [b] May be inverted.

2. Ligand ^{13}C shifts

The relevant results are listed in Table 2. The assignments of the hydrogen-bearing carbons were based on the {^1H} single frequency ^{13}C spectra, thanks to the previous identifications [1,3] in the proton spectra of both III and IV. The assignment of the quaternary carbon atoms is more difficult, it is unambiguous for III since an inversion of 4a and 8a would imply abnormally large coordination shifts; one ambiguity remains, however, for IV.

Group VIB metal carbonyl complexes usually show a small downfield shift for ^{13}C adjacent to coordinating nitrogen [6,8]; this is found here also for TAP itself, where the coordination shift $\Delta\delta$ is 2.1 ppm for C(3) and C(6), and for HAT where the $\Delta\delta$ is 1.4 ppm for the same carbon atoms. Similar, though smaller shifts are found for the other adjacent carbon atoms 4a and 4b. Interestingly, carbon atoms *meta* to the coordination site show a small upfield shift. There is also a small increase of $^1J(^{13}C-^1H)$ on complexation.

Experimental

The spectra were recorded on a Bruker WP80 spectrometer at 20.15 MHz in Fourier Transform Mode with field frequency lock on the solvent. The spectral width was 5550 Hz for 16 K or 32 K data.

The saturated solutions of the samples in deuteriochloroform with TMS as internal standard were run in 10 mm sample tubes. Chemical shifts (δ) are given as positive when downfield from TMS, with an accuracy of ±0.03 ppm; coupling constants are accurate within ±0.3 Hz.

The chromium tetracarbonyl complexes of substituted TAP were prepared as described elsewhere [2]. Analytical samples were obtained after dissolution in the minimal amount of dichloromethane, precipitation with excess of n-hexane, and storage of the mixture at −20°C for a few hours.

$(2\text{-Cl-TAP})Cr(CO)_4$ (50%): Found: C, 55.5; H, 2.2; N, 25.9. $C_{14}H_5ClCrN_4O_4$ (mol.wt. 380.7) calcd.: C, 55.4; H, 2.3; N, 25.9%. ^1H NMR ($CDCl_3$, 100 MHz): 9.56s, 9.56d, 9.05d, J 2.6 Hz; 8.32d, 8.44d, J 9.6 Hz.

(9-CH_3O-TAP)$Cr(CO)_4$ (53%): Found: C, 48.0; H, 2.1; N, 14.8. $C_{15}H_8CrN_4O_5$ (mol.wt. 376.2) calcd.: C, 47.9; H, 2.1; N, 14.9%. ^1H NMR ($CDCl_3$, 100 MHz): 9.62d, 9.36d, 9.01d, 8.91d; *J* 2.6 Hz; 7.56s, 4.31s.

(9-$C_5H_{10}N$-TAP)$Cr(CO)_4$ (75%): Found: C, 53.4; H, 4.0; N, 16.9. $C_{19}H_{15}CrN_5O_4$ (mol.wt. 429.3) calcd.: C, 53.1; H, 3.5; N, 16.3%. ^1H NMR ($CDCl_3$, 100 MHz): 9.52d, 9.21d, 8.93d, 8.81d; *J* 2.6 Hz; 7.47s, 3.58m, 1.81m.

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References

1 R. Nasielski-Hinkens, D. Maetens and D. Vandendijk, Bull. Soc. Chim. Belges, 88 (1979) 169.
2 D. Maetens, J. Nasielski and R. Nasielski-Hinkens, J. Organomet. Chem., 168 (1979) 177.
3 R. Nasielski-Hinkens, M. Benedek-Vamos, D. Maetens and J. Nasielski, J. Organomet. Chem., 217 (1981) 179.
4 G.R. Dobson and K.J. Asali, J. Amer. Chem. Soc., 101 (1979) 5433.
5 L.H. Staal, D.J. Stufkens and A. Oskam, Inorg. Chim. Acta, 26 (1978) 255.
6 P.S. Braterman, D.W. Milne, E.W. Randall and E. Rosenberg, J. Chem. Soc. Dalton, (1973) 1027.
7 B.E. Mann, J. Chem. Soc. Dalton, (1973) 2012.
8 C. Overton and J.A. Connor, Polyhedron, 1 (1982) 53.
9 R. Nasielski-Hinkens et al., to be published.