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3,3′-Bipyridazine: the 'Second-best' Bidiazine Ligand for $M(CO)_4$ Fragments ($M = Cr, Mo, W$)

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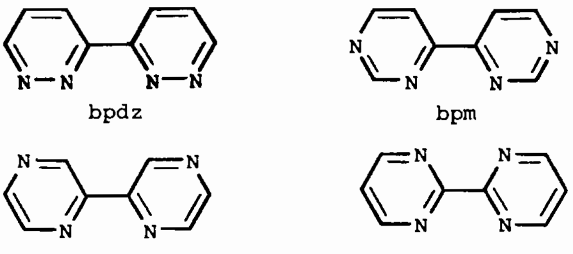
Abstract

Owing to its relatively high basicity ($pK_{a1} = 3.37$), the title ligand yields $M(CO)_4$ chelate complexes ($M = Cr$, Mo, W) which have both metal-to-ligand charge transfer absorption maxima at longer wavelengths than corresponding 2,2′-bipyrimidine and 2,2′-bipyrazine compounds. After 4,4′-bipyrimidine, 3,3′-bipyridazine is the second-best π acceptor among the symmetrical bidiazines with α-diimine structure.

Introduction

We have recently shown that among the four symmetrical bidiazines with α-diimine coordination arrangement (Scheme 1) it is the 4,4′-bipyrimidine (bpm) isomer which exhibits the most effective π acceptor behaviour towards d^6 metal fragments because of its low-lying π^*-orbital in conjunction with relatively good σ bonding properties [1]. During a systematic investigation of the ligands (Scheme 1) we became interested in synthesizing and studying the hitherto unreported tetracarbonylmetal complexes of chromium, molybdenum and tungsten with 3,3′-bipyridazine (bpdz), a ligand with a rather high-lying π^* level [1]. Surprisingly, it turns out that bpdz exhibits superior back-bonding qualities relative to the well-studied isomers 2,2′-bipyrimidine (bpym) [2, 3] and 2,2′-bipyrazine (bpz) [4], as indicated by long-wavelength charge transfer absorptions in $M(CO)_4$ complexes; we report here these results together with an explanation for this unexpected behaviour.



Scheme 1

Experimental

Reactions and measurements involving organometallic compounds were carried out under argon in dried solvents and under subdued light [5].

Instrumentation

^1H NMR: Bruker WH 270, solvent or TMS as internal standard. IR: Perkin Elmer 283B, solution spectra in THF. UV–Vis: Pye-Unicam SP 1800. Cyclic voltammetry: PAR system 173/175, glassy carbon working electrode, saturated calomel reference electrode (SCE), 0.1 M solution of tetrabutylammonium perchlorate in dry dimethylformamide (DMF) as electrolyte. Concentration of complexes during measurement was about 10^{-3} molar, 100 mV/s scan rate.

3,3 -Bipyridazine was synthesized according to Lafferty and Case [6]; repeated sublimation proved to be necessary to purify the material. ^1H NMR ($CDCl_3/DMSO\text{-}d_6$) δ 7.77 (dd, H_5), 8.72 (dd, H_4), 9.27 (dd, H_6); $J_{4,5} = 8.5$ Hz, $J_{4,6} = 1.8$ Hz, $J_{5,6} = 4.5$ Hz. The pK_a was determined according to the method of Crutchley, Kress and Lever [7] at λ_{max} (bpdz) = 260 nm, the procedure yielded $pK_a = 3.37 \pm 0.27$.

The complexes were synthesized by thermal reactions of the photolytically generated $M(THF)(CO)_5$ complexes with the ligands as described previously [1]. In all instances, the formation of red intermediates was observed, presumably N^1-coordinated pentacarbonyl metal complexes [1, 9]. The compounds were purified by column chromatography at Florisil (Merck), elemental analyses and ^1H NMR spectra show that the complexes crystallize as monotetrahydrofuranates from THF/hexane.

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TABLE I. Redox Potentials E (V *vs.* SCE)[a] and Charge Transfer Absorption Maxima λ^{MLCT} (nm) of (bpdz)M(CO)$_4$ Complexes (M = Cr, Mo, W)

Complex	E_{ox}	$E_{\text{red(1)}}$	$E_{\text{red(2)}}$	$\lambda_{\text{max}}^{\text{MLCT(1)}}$		$\lambda_{\text{max}}^{\text{MLCT(2)}}$	
				THF[b]	C_7H_8[c]	THF[b]	C_7H_8[c]
(bpdz)Cr(CO)$_4$	+0.51	−1.19	−2.05[d]	588	626	440	479
(bpdz)Mo(CO)$_4$	+0.7[e]	−1.09	−1.93[d]	552	580	398	405
(bpdz)W(CO)$_4$	+0.7[e]	−1.04	−1.85[d]	560	590	415	440

[a] Potentials from cyclovoltammetry at a glassy carbon electrode in DMF/0.1 M Bu_4NClO_4, 100 mV/s scan rate. [b] Tetrahydrofuran; identical values were obtained in ethanol. [c] Toluene. [d] Irreversible step; cathodic peak potential given. [e] Irreversible step; anodic peak potential given.

TABLE II. Molecular Orbital Energies[a], Redox Potentials[b] and Charge Transfer Absorption Maxima[c] of the Bidiazines and of their Tetracarbonylchromium(0) Complexes

	Ligand				Cr(CO)$_4$ complex				
Ligand	ϵ_{LUMO}	ϵ_{SLUMO}	$\Delta\epsilon$	E_{red}	E_{ox}	E_{red}	ν_{max}^1	ν_{max}^2	$\Delta\nu$
bpym	−0.518	−0.781	0.263	−1.73	not reported[d]		18080[d]	24750[d]	6670
bpz	−0.515	−0.740	0.225	−1.67	+0.68	−1.09	16660	24150	7490
bpdz	−0.583	−0.733	0.150	−1.72	+0.51	−1.19	15970	20880	4910
bpm	−0.460	−0.884	0.424	−1.34	+0.64	−0.80	14490	25000	10510

[a] Values $\epsilon(\beta)$ for nitrogen center Coulomb integrals of $h_N = 0.5$. [b] From cyclic voltammetry at a glassy carbon electrode in DMF/0.1 M Bu_4NClO_4; potentials in V *vs.* SCE. [c] Wavenumbers ν (cm^{-1}) in toluene or benzene[d] solution. [d] Ref. 3.

Cr(bpdz)(CO)$_4$

Reaction time 3 h under reflux, yield 64%, copper-coloured crystals. IR (THF): ν_{CO} = 1990, 1895br, 1860 cm^{-1}. ^{1}H NMR (C_3D_6O): δ 7.99 (dd, H_5), 8.75 (dd, H_4), 9.23 (dd, H_6); $J_{4,5}$ = 8.6 Hz, $J_{4,6}$ = 1.5 Hz, $J_{5,6}$ = 4.9 Hz.

Mo(bpdz)(CO)$_4$

Reaction time 2 days at room temperature, yield 49%, dark red crystals. IR (THF): ν_{CO} = 2020, 1900, 1895sh, 1860 cm^{-1}. ^{1}H NMR (C_3D_6O): δ 8.09 (dd, H_5), 8.88 (dd, H_4), 9.29 (dd, H_6); $J_{4,5}$ = 8.7 Hz, $J_{4,6}$ = 1.6 Hz, $J_{5,6}$ = 4.9 Hz.

W(bpdz)(CO)$_4$

Reaction time 3 days under reflux in THF, yield 34%, dark red crystals. IR (THF): ν_{CO} = 1975, 1875br, 1845 cm^{-1}. ^{1}H NMR (C_3D_6O): δ 8.11 (dd, H_5), 8.93 (dd, H_4), 9.72 (dd, H_6); $J_{4,5}$ = 8.7 Hz, $J_{4,6}$ = 1.7 Hz, $J_{5,6}$ = 4.9 Hz.

Results and Discussion

In agreement with the relative basicities of the parent diazines [8], bpdz is the strongest base among the bidiazines (Scheme 1) with pK_{a1} = 3.37; bpz has pK_{a1} = 0.45 [7] and bpm has pK_{a1} = 1.5 [1]. This advantage of bpdz seems to improve the complex stability of coordination compounds, as is evident from the good thermal stability of the Cr(CO)$_4$ complex; corresponding tetracarbonylchromium complexes of bpz [4, 9] and bpm [1] were found to decompose rapidly at room temperature.

For investigation of the π back-bonding behaviour, we have studied the ligand and its M(CO)$_4$ complexes by electrochemistry and electronic absorption spectroscopy (Tables I, II). Cyclic voltammetric experiments (Fig. 1) show that the ligand bpdz and its complexes have relatively negative reduction potentials when compared to corresponding bpym, bpz and bpm species; this result is in agreement with the rather negative LUMO energy calculated by the

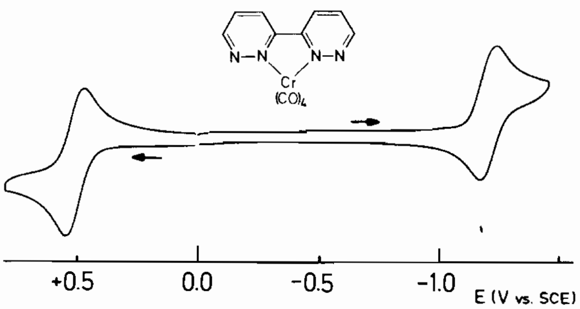

Fig. 1. Oxidative and reductive cyclovoltammogram of Cr(bpdz)(CO)$_4$ in DMF/0.1 M Bu_4NClO_4, 100 mV/s scan rate.

Hückel method (Table II). The reversibility found for the reduction waves indicates that the LUMO is indeed a ligand-centered π^* orbital, an assumption which is further supported by ESR studies of chemically generated anion radical complexes [9]. On the other hand, the low value for the reversible (Fig. 1) Cr(0) → Cr(I) oxidation in $Cr(bpdz)(CO)_4$ demonstrates the effect of the relatively high ligand basicity by destabilization of the highest occupied metal-based orbital; molybdenum and tungsten tetracarbonyl complexes are irreversibly oxidized under these conditions [4].

Accordingly, the low-energy charge transfer absorption bands are shifted more bathochromically than would be expected on the basis of π electron calculations and reduction potentials alone; nevertheless, it is still suprising that these transitions occur at even lower energies than in corresponding bpym and bpz complexes (Table II). The absorption maxima (lg ϵ ~3.6–3.9) show a characteristic solvent dependence (negative solvatochromism) which is indicative of metal-to-ligand charge transfer (MLCT) transitions [10]. Interestingly, the next major transition in the bpdz complexes occurs at relatively low energy (Fig. 2); since Hückel MO calculations (Table II) show that the bpdz isomer has the lowest-lying second-lowest unoccupied molecular π orbital (SLUMO) among the four bidiazines (Scheme 1), we assign this second intense absorption to a d → π^* (SLUMO) transition. The situation of this second band in the visible region also explains the deep purple colour of the $M(bpdz)(CO)_4$ complexes in solution.

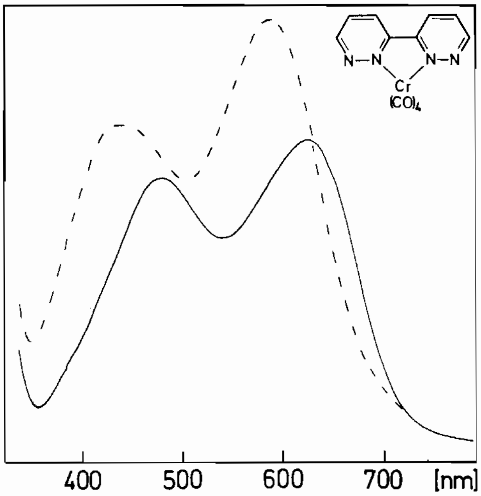

Fig. 2. Absorption spectra of $Cr(bpdz)(CO)_4$ in THF (– – –) and toluene (——).

Summarizing, the good σ bonding capability of the bpdz ligand apparently helps to compensate for the relatively high-lying π^* level by synergistic enhancement of π back donation, thus leaving 3,3′-bipyridazine as the second-best π acceptor ligand for $M(CO)_4$ fragments among the four bidiazines (Scheme 1). This result emphasizes once more the importance of σ donation in the stabilizing function of such ligands for low-valent metal centers.

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