Coordination Chemistry of π-Electron Deficient Ligands. Binuclear Tungsten Pentacarbonyl Complexes of the Weakly Basic 2,1,3-Benzochalcogenadiazoles

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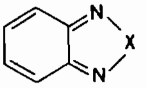
π-Electron deficient heterocycles constitute a very important class of ligands because their complexes with π-electron rich metal fragments exhibit special photo- and electrochemical properties. Resulting from the low-lying ligand-centered π* levels in such systems are:

(i) intense metal-to-ligand charge transfer (MLCT) absorptions, often in the visible region,

(ii) chemical and electrochemical reduction, facilitated by coordination, and

(iii) stabilization of the one-electron reduction products, the complex anion radicals.

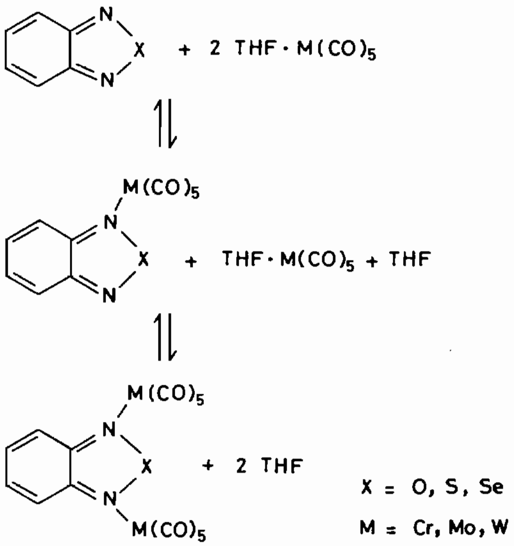
Since double coordination at bifunctional ligands such as pyrazine [1–4], 4,4′-bipyridine [4] or 2,2′-bipyrimidine [5] gives rise to particularly strong effects, we became interested in the coordination chemistry of the related 2,1,3-benzochalcogenadiazoles (1) [6]. These molecules offer several potential coordination sites [6, 7] and less negative reduction potentials [8].



(1)

X = O : 2,1,3-benzoxadiazole (bod)
X = S : 2,1,3-benzothiadiazole (btd)
X = Se: 2,1,3-benzoselenadiazole (bsd)

Recently we have reported electron spin resonance (ESR) studies on mono- and binuclear pentacarbonylmetal(0) complexes (Cr, Mo, W) of the more basic anion radicals bod$^{\cdot-}$, btd$^{\cdot-}$, and bsd$^{\cdot-}$ [6]. However, low basicities of the neutral ligands (bsd: pK_{s_1} = −1.41, pK_{s_2} = −8.10 [9]) prevented the formation of N,N′-dicoordinated binuclear neutral species from photolytically generated solvent–pentacarbonyl complexes in THF. Only mononuclear complexes were obtained [6]. Apparently the basic character of tetrahydrofuran leaves the two-step equilibrium (2) at the intermediate stage.



X = O, S, Se
M = Cr, Mo, W

(2)

By shifting this equilibrium we have now succeeded in synthesizing binuclear pentacarbonyltungsten complexes of the 2,1,3-benzochalcogenadiazoles.

Whereas the mononuclear compounds can be obtained from THF solutions as reported [6], the binuclear complexes were now accessible from the components in eqn. (2) by removing the solvent THF *in vacuo* and by immediately redissolving the residue in toluene. Crystallization after adding hexane afforded the binuclear complexes which were characterized by elemental analysis and spectroscopy (Table I), Table II also shows some data of the mononuclear complexes for comparison.

The most conspicuous feature of the binuclear complexes is their intense absorption at long wavelengths (640–700 nm) which must be attributed to a MLCT transition (dπ → π*) on the basis of solvent dependence, cyclic voltammetric and electron spin resonance results [6]. Figure 1 shows the absorption spectra of the bsd ligand and its mono- and binuclear pentacarbonyl–tungsten(0) complexes in toluene.

The low-energy shifts in the absorption spectra are the consequence of considerably destabilized

TABLE I. Infrared and ^{1}H-NMR Data of Binuclear Complexes.

Complex	ν_{CO} (cm^{-1})^a	δ(ppm)^b
bod[W(CO)$_5$]$_2$	2061, 1955, 1935sh	7.20 (ps)
btd[W(CO)$_5$]$_2$	2062, 1950, 1930sh	7.85 (m, AA′BB′)
bsd[W(CO)$_5$]$_2$	2060, 1942, 1925sh	7.71 (ps)

^{a}Measurements in dichloromethane solution; ^{b}Spectra obtained in CDCl$_3$ solution (270 MHz).

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TABLE II. Electrochemical and UV-Visible Absorption Data.

Complex	E_{red} (V *vs.* SCE)[a]	λ_{max}^{MLCT} (nm)	λ_{max}^{LF} (nm)[b]
bod[W(CO)$_5$]	−0.78 (−0.95)[c]	512	375
bod[W(CO)$_5$]$_2$	[d] (−0.55)	660	375
btd[W(CO)$_5$]	−0.83 (−0.97)[c]	488	400
btd[W(CO)$_5$]$_2$	−0.36 (−0.53)	642	408
bsd[W(CO)$_5$]	−0.76 (−0.84)[c]	518	405
		(546 hexane	413)
bsd[W(CO)$_5$]$_2$	−0.30 (−0.47)	680	405sh
		(704 hexane	415sh)

[a] Data from cyclovoltammetry in dimethylformamide (acetonitrile), 0.1 M $Bu_4N^+ClO_4^-$; glassy carbon working electrode. At 100 mV/s sweep rate all processes were electrochemically reversible. Reduction potentials of ligands in DMF: −1.34 V (bod), −1.39 (V) btd, −1.27 V (bsd); [b] Measurements in toluene, except where indicated; typical extinction coefficients of the MLCT bands are 5 × 10^3 for the mononuclear and 10^4 for the binuclear complexes; [c] Reduction of mononuclear complexes is also observed during experiments with binuclear species (dissociation according to eqn. (2)); [d] Not observed in DMF due to complete dissociation into the mononuclear complex.

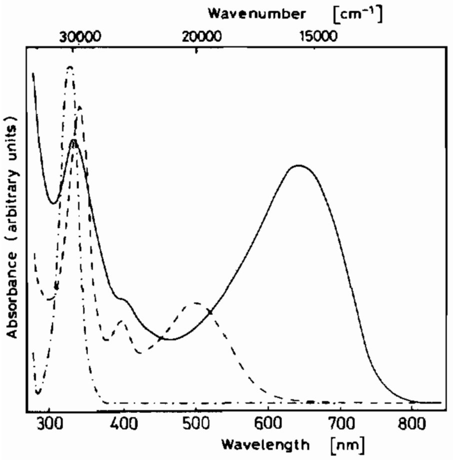
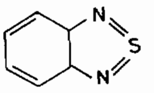


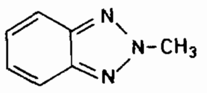
Fig. 1. Absorption spectra of bsd (–·–), bsd[W(CO)$_5$] (– – –) and bsd[W(CO)$_5$]$_2$ (——) in toluene (bsd: 2,1,3-benzoselenadiazole).

π*-levels after single and, in particular, after double coordination. The reduction potentials as measured by cyclic voltammetry increase (Table II) by about 0.5 V for the first and by *ca.* 0.4 V for the second coordination step. Additional features in the electronic absorption spectra of the complexes include the virtually solvent-independent [10] ligand-field (LF, d → d*) and intra-ligand (IL, π → π*) transitions.

The use of coordinating solvents in electrochemistry has allowed us to observe the dissociative lability of the binuclear complexes according to eqn. (2). Typically, the lability (and the potentials) are somewhat larger in dimethylformamide (DMF) than in acetonitrile (Table II). Similar sequences can be obtained by comparing the different ligands: complexes with the selenium ligand bsd are more persistent, easier to reduce, and more deeply coloured than are their oxygen or sulfur counterparts. The relatively high lying π* level of the sulfur system btd probably has its origin in a significant contribution of the sulfur–diimine [7] resonance structure which stabilizes this molecular orbital.



btd



mbt

While the benzochalcogenadiazoles exhibit such a versatile [6, 7] organometallic coordination chemistry, the related 2-methyl-1,2,3-benzotriazole (mbt) do not undergo complexation under these conditions, the reason being either some steric interference with the N-methyl group, or an even further lowered basicity. However, the main group VI analogues (1) seem to be promising ligands for π-electron rich inorganic and organometallic electrophiles. We are continuing to investigate their potential as π-electron deficient bridges between metal fragments.

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