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Intermolecular Interaction of Tris-bipyridyl Metal Complexes, $M(bpy)_3$ (M = Al, V, Fe), with Tetracyanoethylene

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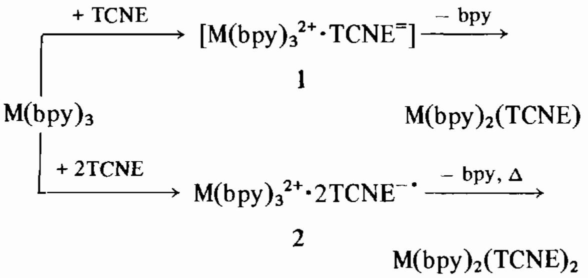
Previously, we reported that the tris-bipyridyl low-valent metal complexes, $M(bpy)_3$ (M = Ti, Zr, V; bpy = 2,2′-bipyridine, $C_{10}H_8N_2$), promote a variety of autocondensation reactions of tetracyanoethylene (C_6N_4, TCNE) [1]. In the first step a two-electron transfer is involved from the electron-rich $M(bpy)_3^0$ species to TCNE. Either the dianion, $TCNE^{2-}$, or the radical monoanion, $TCNE^{-\bullet}$, are so produced depending on the $M(bpy)_3$/TCNE ratio, according to the following scheme



Recently, donor–acceptor charge transfer complexes (DA) containing polycyano anions have been the subject of intensive investigations [2], especially the ion radical salts of $TCNE^{-\bullet}$ [3], which in combination with another radical as counteraction can give mixed stacks ....$D^\bullet A^\bullet D^\bullet A^\bullet$.... where a ferromagnetic coupling dominates. This precedent prompted us to investigate the salts **1** or **2** of the above scheme. We have succeeded in isolating and studying only the ion radical salts **2** for M = Al, V, Fe. Unfortunately such complexes, pure and crystalline in the solid state, decompose slowly in solution even under dinitrogen, because of the replacement of one bipyridine ligand by $TCNE^{-\bullet}$, preventing us from obtaining good quality crystals for an X-ray diffraction study. Nevertheless, from the chemico-physical measurements (magnetism, IR and electronic spectra), we may suggest a hypothetical novel spatial arrangement of the ions in the salts $M(bpy)_3^{2+}\cdot 2TCNE^{-\bullet}$, which we present here.

Experimental

Starting Materials

$Al(bpy)_3$ [4], $V(bpy)_3$ [1c] and $Fe(bpy)_3$ [5] were prepared as outlined in the literature or as previously reported; TCNE was used as received from Fluka.

Standard Procedure for the Synthesis of $M(bpy)_3^{2+}\cdot 2TCNE^{-\bullet}$

$Fe(bpy)_3$ (3.0 g, 5.72 mmol) was dissolved in thf (dehydrated and freshly distilled, 100 ml). Solid TCNE (1.47 g, 11.47 mmol) was added under dinitrogen. After about 30 min of stirring, a dark red crystalline product was formed, which was filtered and washed with thf (3.2 g, 72%).

Results and Discussion

We recall some pertinent information available in the literature concerning the solid state structures of $TCNE^{-\bullet}$ ion radical salts. This species is generally found as a free radical anion or as a diamagnetic π dimer. In both cases, the solid-state structure is determined by the tendency of $TCNE^{-\bullet}$ to interact via π electrons with either itself or some other vicinal planar π molecule.

(i) π dimers, $(TCNE^{-\bullet})_2$ have been postulated in the structures of alkali tetracyanoethylenides from the strong absorption band at 540 nm assigned to a charge transfer between two parallel and close $TCNE^{-\bullet}$ moieties [6]. The same dimer, slightly distorted and stacked in segregated linear chains, has been found in the structure of $TCNE^{-}\cdot$1,1′-trimethylenferrocenophane [7].

(ii) A sandwich $TCNE^{-\bullet}C^{2+}TCNE^{-\bullet}$ arrangement (where C^{2+} is the diamagnetic $[Cp_2Ti(p\text{-}TCD)]_2^{2+}$), containing the free radical $TCNE^{-\bullet}$ interacting via the π electrons with the planar *p*-TCD moiety (*p*-TCD = *para*-tolyloxalylamidine), has been deduced from the magnetic molar susceptibility data, which corresponds to two unpaired electrons [8].

(iii) Mixed stacks of radical cation $C^{+\bullet}$ and $TCNE^{-\bullet}$ have been found in the ferrocinium salts $C^{+\bullet}\cdot TCNE^{-\bullet}$ ($C^+ = Fe(C_5H_5)_2^+$ [9], $Fe(Me_5C_5)_2^+$ [3b]), where the π interaction between $TCNE^{-\bullet}$ and the cyclopentadienyl ring is prevalent, causing an ordering of the unpaired electrons (μ = 3.10 BM at 300 K [3b]).

In the title compounds $TCNE^{-\bullet}$ may interact via π electrons either with the coordinated bpy or with itself. The former kind of interaction probably prevails, with the two $TCNE^{-\bullet}$ radicals lying close to one other on two orthogonal planes, parallel to the bpy planes respectively, as depicted in Fig. 1. A

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TABLE I. Analyses[a], Diffuse Reflectance Spectra[b] and Magnetic Susceptibility Data[c] for the Salts $M(bpy)_3^{2+}\cdot(TCNE^{-})_2$

Compound	Found (calc.) (%)				λ_{max} (nm) and Assignment		μ_{eff} (BM)
	C	H	N	M	M → bpy	$TCNE^{-}$ → bpy	
$Al(C_{10}N_2H_8)_3(C_6N_4)_2$	66.85 (67.11)	3.30 (3.22)	26.23 (26.08)	3.61 (3.59)		390	2.06
$V(C_{10}N_2H_8)_3(C_6N_4)_2$	64.73 (65.03)	3.28 (3.12)	25.10 (25.28)	6.78 (6.57)	645	400	3.83
$Fe(C_{10}N_2H_8)_3(C_6N_4)_2$	64.45 (64.63)	3.24 (3.10)	25.20 (25.12)	7.08 (7.15)	520	385	diamagnetic

[a] By Malissa and Reuter Analytische Laboratorien. [b] On MgO-diluted samples. [c] By the Gouy method at 295 K.

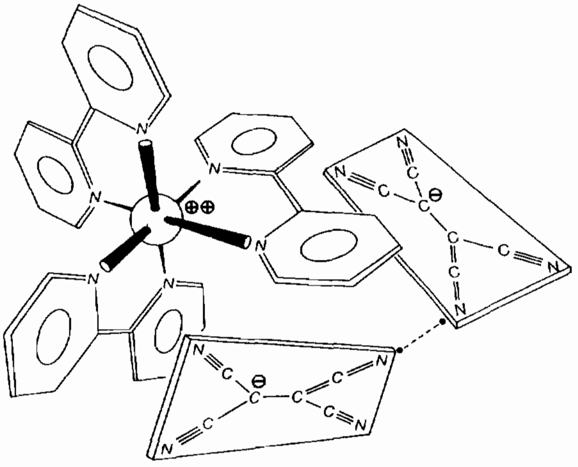

Fig. 1. Hypothetical spatial arrangement of the ions in the salts $[M(bpy)_3^{2+}\cdot 2TCNE^{-\bullet}]$.

diamagnetic σ dimer is formed, $(CN)_2\bar{C}-(CN)C{=}C{=}N-N{=}C{=}C(CN)-\bar{C}(CN)_2$, as a consequence of a positive overlap between the two orbitals, bearing the antiferromagnetically coupled unpaired electrons centred on the two close nitrogen atoms. All the experimental data support such a conclusion; first of all there is no doubt that $TCNE^{-\bullet}$ is dimerized, because it does not provide any contribution to the molar magnetic susceptibility (Table I). The dimer present is certainly not a π dimer, because the electronic spectrum does not show the strong absorption at 540 nm, due to the charge transfer between the two parallel $TCNE^{-\bullet}$ [6]. Conversely, the electronic spectrum reveals the interaction between $TCNE^{-}$ and bpy in the sense that it shows an intense band at 390 nm, which is absent in solution (Fig. 2), probably arising from the charge transfer $TCNE^{-}$ → bpy (the structured band, centred at 415 nm in solution, is typical of free $TCNE^{-\bullet}$ [6]). Finally the IR spectrum in the ν(C≡N) stretching vibration region is also conclusive: usually this region is considered of diagnostic value for ascertaining both the charge and the coordination mode of TCNE [2g, 3c]. Non-coordinated $TCNE^{-\bullet}$ gives only two peaks at 2140, 2180 cm^{-1} in solution (Fig. 3), shifted by 3–5 cm^{-1} in the solid state, irrespective of the type of π interaction present [2g, 3b, 3c, 7, 8], assignable to ν_9 and ν_{15} in D_{2h} [10]. The presence of more than two peaks, up to a maximum of four, is indicative of TCNE coordination to a metal centre (M) through a nitrogen atom: $M \leftarrow N{\equiv}C{-}C(CN){=}C(CN)_2$ [11]. Precisely four well-resolved peaks are visible (Fig. 3) and $TCNE^{-\bullet}$ is certainly non-coordinated (in the salts 2, $TCNE^{-\bullet}$ can be replaced quantitatively by the anion $B(C_6H_5)_4^{-}$). We believe that the four peaks are the

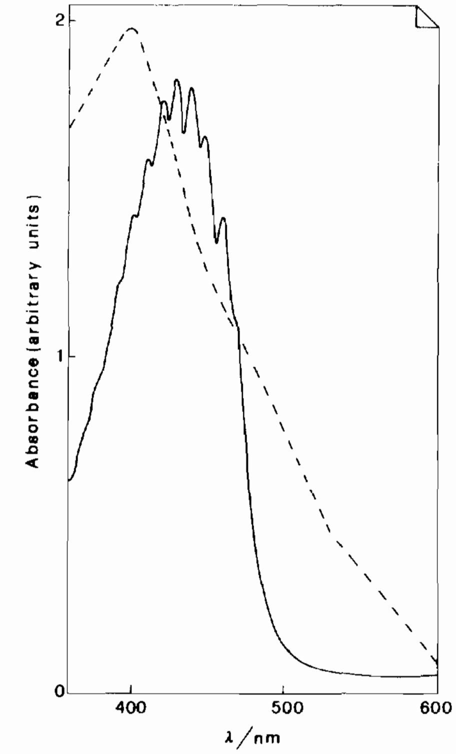

Fig. 2. Electronic absorption spectra of $[Al(bpy)_3^{2+}\cdot 2TCNE^{-\bullet}]$; —— acetonitrile solution, – – – diffuse reflectance. The spectra of the other title salts (M = V, Fe) are identical to this one apart from the extra M → bpy charge transfer band (see Table I).

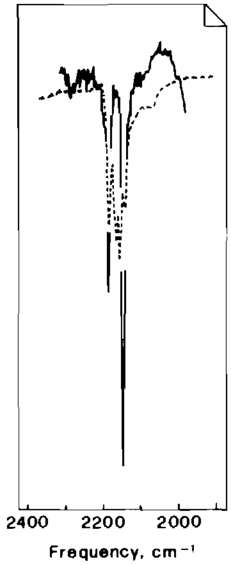

Fig. 3. Infrared spectra of [V(bpy)$_3^{2+}$·2TCNE$^{-\cdot}$]; —— thf solution, - - - - nujol mull; the spectra of the other less soluble title salts (M = Al, Fe) are superimposable to this one.

expected ν(C≡N) stretching vibrations (ν_1, ν_9, ν_{15}, ν_{19} [10]) infrared active in a reduced symmetry for TCNE$^{-\cdot}$, as expected for coordination to a metal centre through a nitrogen atom, again an argument favouring the formula depicted in Fig. 1.

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