relative configuration is assigned on the basis of the argument advanced in the text. The C-2–C-3 erythro configuration is assigned by analogy to the known stereochemical outcome of a related reaction of this aldehyde.[1]

(15) C. T. Buse and C. H. Heathcock, *J. Am. Chem. Soc.*, **99**, 8109 (1977).

(16) The stereostructure of **17** was determined by single-crystal X-ray analysis: J. A. Bertrand and D. VanDerveer. That **15** and **17** have the same relative stereochemistry at the pertinent centers was shown by converting them into the same β-hydroxy aldehyde. The sequence of reactions for this conversion is reduction with lithium aluminum hydride in ether; removal of the trimethylsilyl group; cleavage of the resulting vicinal diol with $NaIO_4$ in aqueous ethanol. Full details fo the X-ray determination on **17** and on the correlation of **15** with **17** will be reported in a full paper.

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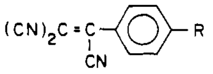
The Intermolecular π-Amphoteric Character of *p*-Tricyanovinyldimethylaniline

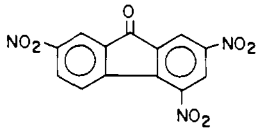
Sir:

While, in principle, any molecular species may behave as a "donor" or "acceptor" in complex formation, the behavior of a given species will depend not only on its own ionization potential (IP_g) and electron affinity (EA_g) but also on those of its complexing partner, as well as the specific experimental conditions under which the molecules interact. In this communication, we demonstrate for the first time that an organic *molecule*, *p*-tricyanovinyldimethylaniline[1] (TCVDMA, **1**), forms a *solid* complex with one molecular partner in which it behaves as a donor and a *solid* complex with another molecular partner in which it behaves as an acceptor.[2,5,6] Thus, this is also the first report of the isolation of solid complexes of TCVDMA. A previous report[7] indicates possible intermolecular complex formation in *solution*.



1 R= $-N(CH_3)_2$

2 R= $-C(CN)_2^-$



3

In the course of our[8] characterization of the donor properties of the *p*-tricyanovinylphenyldicyanomethide[9] ($TCVPDM^-$, **2**), we noted a molecular analogy in the electrochemical behavior of TCVDMA and $TCVPDM^-$. Since $TCVPDM^-$ forms a complex with 2,4,7-trinitrofluorenone (TNF, **3**),[8] we were prompted to prepare the TNF complex of TCVDMA, which crystallizes from ethanol solution as red plates of 1:1 stoichiometry, mp 151 °C dec.

We also attempted to prepare the TNF complex of TCVDMA in aromatic solvents where relatively large solvent shifts of the absorption maximum of TCVDMA have been observed.[1] To our surprise, we found that TCVDMA crystallized from a variety of aromatic solvents, including *N,N*-dimethylaniline (DMA), complexed with the solvent.[10] We established the stoichiometry of the purple DMA complex as DMA·4TCVDMA,[11] mp 138 °C dec, by solution spectrophotometry. Analytical and crystal data for the TCVDMA complexes of TNF and DMA are given in Table I. The observation of a lattice constant ~4.0 Å in DMA·4TCVDMA (Table I) is reminiscent of that found in uniform segregated stack structures of ion-radical salts;[3,12] we have also observed a comparable short lattice constant in the 1,2,4-trichlorobenzene complex of TCVDMA which also has a 1:4 stoichiometry.[10]

Table I. Analytical[a] and Crystal Data[b] for TCVDMA Complexes

	TCVDMA·TNF		DMA·4TCVDMA	
	calcd	obsd	calcd	obsd[c]
C	58.11	57.78	71.43	71.41
H	2.81	3.04	4.96	5.29
N	18.24	18.00	23.61	22.80
a, Å	7.467 (1)		3.992 (6)	
b, Å	11.992 (1)		16.315 (10)	
c, Å	14.405 (1)		20.562 (11)	
α, deg	107.02 (1)		90	
β, deg	102.49 (1)		90.27 (9)	
γ, deg	91.38 (1)		90	
V_{mc}[d,e], Å^3	1198.9		1339	
V_{add}[d,e], Å^3	1229.6		1411	
Z	2		1	
ρ_{calcd}	1.487		1.214	
ρ_{obsd}	1.49 (1)		1.23 (1)	

[a] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. [b] Lattice constants were determined by Molecular Structure Corporation, College Station, Texas, using Cu Kα radiation. [c] Complexes of TCVDMA with volatile components such as DMA cannot be washed with solvents or vacuum dried without loss of the volatile component. [d] Reference 3. [e] Molecular volume of TCVDMA from Chetkina. L. A., Popova, E. G.; Kotov, B. V.; Ginzburg, S. L.; Smelyanska, E. M. *J. Struct. Chem.* **1976**, *17*, 902, Molecular volume of TNF from Dorset D. L.; Hybl, A.; Ammon, H. L. *Acta Crystallogr., Sect. B* **1972**, *28*, 3122. Molecular volume of DMA calculated from room temperature density.

Table II. Molecular Energy Levels and Redox Potentials

molecule	IP_g, eV	EA_g, eV	$E_{1/2}^{ox}$ [a]	$E_{1/2}^{red}$ [a]
DMA	7.45[b]	1.24[c]	+0.71[c]	<−1.0
TCVDMA	7.94[e]		+0.96[f]	−0.70[f]
TNF		2.1[g]	>+1.6	−0.42[h]

[a] Measured in acetonitrile solution in volts vs. a saturated calomel electrode. [b] Egdell, R.; Green, J. C.; Rao, C. N. R. *Chem. Phys. Lett.* **1975**, *33*, 600. [c] Jordan, K. D.; Barrow, P. D. *Acc. Chem. Res.* **1978**, *11*, 341. [d] Seo, E. T., et al. *J. Am. Chem. Soc.* **1966**, *88*, 3498. This value is the potential as half peak height for an irreversible anodic wave. [e] This value is reported in ref *b* for *p*-nitrodimethylaniline. [f] Kuder, J. E.; Limburg, W. W.; Pochan, J. M.; Wychick, D. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1643. [g] Chen, E. M. C.; Wentworth, W. E. *J. Chem. Phys.* **1975**, *63*, 3183. [h] Kuder, J. E.; Pochan, J. M.; Turner, S. R.; Hinman, D. T. *J. Electrochem. Soc.* **1978**, *125*, 1750.

Our designation of TCVDMA as the donor in its TNF complex and as the acceptor in its complex with DMA is in accord with the available data, summarized in Table II, concerning ionization energies, electron affinities, and redox potentials of these molecules. Thus, from Table II, TCVDMA is more easily oxidized and less readily reduced than TNF and it is less easily oxidized and more easily reduced than DMA. The data of Table II are necessary but not sufficient conditions for the isolation of the new complexes described herein. The tendency of TCVDMA to complex with aromatic solvents is a major reason for this statement. The presence of the strongly electron-attracting tricyanovinyl group in a molecule is not a sufficient condition for solid complex formation with DMA. Both 3-tricyanovinylindole (peak of irreversible cathodic wave at −0.60 V vs. SCE, conditions as in Table II) and 4-tricyanovinyl-2,6-dimethylphenol (peak of irreversible cathodic wave at −0.50 V vs. SCE, as above) crystallize unchanged from DMA, in contrast to the behavior of TCVDMA and TNF noted herein.

Distinct charge-transfer maxima separated from the absorption of the components are not observed for these complexes, a situation also seen with TCVPDM$^-$,[8] owing to the intense visible absorption of those species.[1,9] However, for TCVDMA·TNF, spectra in ethanol solution and in KBr pellets reveal absorption at wavelengths >750 nm not due to either component of the complex and assigned to the tail of a charge-transfer absorption band. A further attempt to observe a charge-transfer maximum in TCVDMA·TNF was made. In 0.5-mm-path-length cells, a 10^{-3} M solution of TCVDMA in ethanol or chloroform gave a level base line. Portionwise solution of TNF in the sample cell gave new absorbance in both cases between 500 and 530 nm, with maxima at 517 nm in ethanol and 502.5 and 527.5 nm in chloroform attributed to charge-transfer absorption.[14] Charge-transfer absorption between DMA and TCVDMA was observed as follows. In chloroform solution, 10^{-3} M in TCVDMA, a "window" in the absorption spectrum is apparent between 350 and 400 nm. Portionwise addition of DMA up to a concentration of 10^{-2} M in this solution reveals new absorption with absorbance increasing from 0.04 at 390 nm to 0.44 at 350 nm; however, no maximum was observed in this region. The new absorption, which we assign to charge-transfer absorption in both DMA·4TCVDMA and TCVDMA·TNF, is at energies expected[15] for molecular species with the energy levels and redox potentials listed in Table II.

In summary, we have demonstrated the π-amphoteric character of TCVDMA by its formation of solid complexes with TNF where it functions as a donor and with DMA where it functions as the acceptor in a solid complex of rare 1:4 stoichiometry. New absorption attributed to complex formation has been observed for each of the new complexes. A potential outgrowth of this work might be the use of π-amphoteric molecules to form new classes of complexes with three interacting components.[3] Our attempts to use TCVDMA to form three-component complexes with DMA and TNF have led only to the isolation of mixtures of the two-component complexes of these compounds to date.

Acknowledgments. The authors thank G. T. Fekete for X-ray powder diffraction patterns of the materials discussed herein and K. Fuller and K. Graham for typing the manuscript.

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Oxygenation of Cobalt(II) Carboranylporphyrinates: Solid-State, Nonaqueous, and Aqueous Solutions

Sir:

Oxygenation studies[1] of cobalt(II) porphyrinate complexes have ranged from simple porphyrins[2-7] like $\mathrm{L\cdot Co^{II}\{TPP\}}$[8] to porphyrins with more elaborate peripheral substitution such as the elegant "picket fence" cobalt(II) porphyrinate, $\mathrm{L\cdot Co^{II}\{TpivPP\}}$ of Collman and co-workers.[9] We report here the reaction of certain cobalt(II) carboranylporphyrinate complexes with molecular oxygen in the solid state, in solution in organic solvents, and in aqueous solution.

The crystalline porphyrin $\mathrm{MeIm\cdot Co^{II}\{TpivPP\}}$ reversibly binds O_2 with $P_{1/2}^{O_2} = 8.1$ kPa.[9] Although no solid-state $P_{1/2}^{O_2}$ values were determined for the porphyrins described here, the EPR spectra provide good estimates of the extent of oxygenation. The tetra-meso-substituted porphyrins $\mathrm{ar\cdot Co^{II}\{P(CH_2C_2B_{10}H_{10}Me)_4\}}$[10] (**1**), $\mathrm{ar\cdot Co^{II}\{P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4\}}$[11] (**2**), $\mathrm{\alpha^4\cdot Co^{II}\{P(C_6H_4NHCOCH_2C_2B_{10}H_{11})_4\}}$[12] (**3**), $\mathrm{ar\cdot Co^{II}\{P(C_6H_4NHCOCH_2C_2B_9H_{11}\cdot pipH)_4\}}$[13] (**4**), and $\mathrm{\alpha^4\cdot Co^{II}\{P(C_6H_4NHCOCH_2C_2B_9H_{11}\cdot pipH)_4\}}$[13] (**5**) were prepared by reaction of the free base[13b] with anhydrous $CoCl_2$ and 2,6-lutidine as proton scavenger[14] in THF and identified by elemental analysis[15] and/or visible spectra and EPR. The pentametalloporphyrin $\mathrm{ar\cdot Co^{II}\cdot\{P[C_6H_4NHCOCH_2C_2B_9H_{10}Rh^{III}(H)(PPh_3)_2]_4\}}$[16] (**6**) was prepared in very good yield by reaction of **4** with 4 equiv of $\mathrm{(Ph_3P)_3RhCl}$[17] in refluxing EtOH.

The solid-state oxygenation of **1–4** and **6** was investigated after preparation of the five-coordinate MeIm complexes under N_2 and determination of the EPR spectrum of the deoxy species ($g \approx 2.3$) at room temperature. After evacuation the sample was exposed to ~100 kPa of O_2 for 6–24 h at ~22 °C before the EPR spectrum was recorded again. During this time the deoxy signal diminishes and the oxy signal ($g \approx 2.0$) increases in intensity.[18] Figure 1 shows the EPR spectra of MeIm·**1** and the MeIm·**6**, respectively, under ~100 kPa of O_2. The figures show that the majority of the cobalt sites are oxygenated under these conditions and both porphyrins have a similar extent of oxygenation even though the peripheral substituents of **6** are many times larger than those of **1.** The atropisomeric purity seems to have relatively little effect on the extent of oxygenation with **3**·MeIm having only a slightly higher affinity for O_2 than **2.** In contrast, no reaction was detectable by EPR when crystalline $\mathrm{MeIm\cdot Co^{II}\{TPP\}}$ was exposed to ~100 kPa of O_2. The oxygenation reactions are reversible (high vacuum, ~50 °C, 12 h) except in the case of **6** which had EPR absorptions remaining in the $g = 2$ region after the deoxygenation treatment. From these observations we conclude that an important factor in the reversible oxygenation of solid cobalt(II)[18b] porphyrinates is the ease of access of O_2 to the cobalt site with the bulk and orientation of the peripheral protection apparently having little effect on the extent of oxygenation.

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