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Tetracyanoethylene Anion as a Hard σ Base. Synthesis and Structure of the 1 : 1 Adduct of Tetracyanoethylene and Bis(π-cyclopentadienyl)vanadium Monobromide

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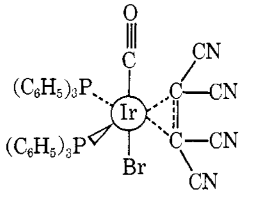
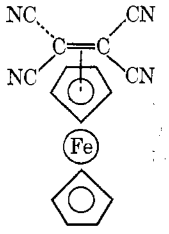
Reaction of $(\pi\text{-}C_5H_5)_2VX$ (X = Cl, Br, I) with tetracyanoethylene (TCNE) gives rise to the 1:1 adducts $(\pi\text{-}C_5H_5)_2VX \cdot TCNE$. The infrared spectra of the adducts are nearly identical and are the same in both the solid and solution phases. A single-crystal X-ray study of the bromo adduct shows that TCNE has added to vanadium through a nitrile nitrogen, rather than through the π-olefinic bond. Thus, the coordination about vanadium is distorted tetrahedral, and the mode of TCNE attachment is different from all previously known transition metal–TCNE complexes. The adducts are best represented as formal vanadium(IV) complexes of tetracyanoethylene anion. This conclusion is reached on the basis of the low C≡N and C=C stretching frequencies. The details of the molecular structure suggest an intramolecular Br^-–TCNE interaction. The observed structure is consistent with a hard acid ($(\pi\text{-}C_5H_5)_2VX^+$)–hard base ($TCNE^-$) interaction, in contrast to the previous structures of TCNE complexes involving soft acid (TCNE)–soft base (metal complexes) interactions. The crystals studied belonged to space group Pccn with a_0 = 21.09 (4), b_0 = 11.68 (2), and c_0 = 12.79 (2) Å. The observed density was 1.64 g/cm³, giving a calculated value of 8.01 formula units in the cell. The structure was solved using 577 visually estimated unique reflections and refined to a final *R* factor of 13.0% based on *F*.

Introduction

Earlier workers have shown that tetracyanoethylene reacts with certain organometallic and inorganic complexes of iridium,[1,2] rhodium,[2] platinum,[3] palladium,[4] and chromium.[5] Reactions of TCNE with ferrocene,[6] cobaltocene,[7] and dibenzenechromium[8] have also been described. Crystal structure determinations for $IrBr(CO)(P(C_6H_5)_3)_2TCNE$[9] and for the 1:1 ferrocene–TCNE adduct[10] have been reported.[10a] In the iridium complex I the TCNE ligand is bonded to iridium through the central carbon–carbon "double" bond, which is considerably longer than the double bond in TCNE.[11] In this complex, the four C≡N groupings are bent away from the iridium atom, so that the TCNE moiety is no longer planar. The ferrocene–TCNE adduct II seems to be a typical charge-transfer complex of TCNE, with the TCNE acceptor stacked between donor cyclopentadienyl rings of different ferrocene molecules. The Pt, Pd, Rh, and Cr complexes all appear to be structurally similar to $IrBr(CO)(P(C_6H_5)_3)_2TCNE$ insofar as the metal–TCNE bonding is concerned. Each of these complexes exhibits a single C≡N stretching vibration, which may be taken as diagnostic of π-olefin type metal–TCNE bonding. The cobaltocene and dibenzenechromium reaction products are not similar to ferrocene–TCNE, since in these cases complete charge transfer with formation of TCNE radical anion has been demonstrated.[7,8]



I



II

Since no investigations of the reactions of TCNE with vanadocene, chromocene, or any of their derivatives had been reported, we undertook the present investigation with the hope of discovering interesting new aspects of TCNE chemistry. In contrast to ferrocene, none of the compounds vanadocene, chromocene, or $(\pi\text{-}C_5H_5)_2VX$ (X = Cl, Br, I) obeys the effective atomic number rule.[12] All of the latter compounds have fewer than 18 electrons in the valence shell and might therefore be expected to react with TCNE to form a metal–TCNE bond, rather than a ring–TCNE charge-transfer complex. The vanadium and chromium organometallics also would be expected to undergo oxidation by the relatively strong oxidant TCNE.[13]

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(1) W. H. Baddley, *J. Am. Chem. Soc.*, **90**, 3705 (1968).

(2) W. H. Baddley, *ibid.*, **88**, 4545 (1966).

(3) W. H. Baddley and L. M. Venanzi, *Inorg. Chem.*, **5**, 33 (1966).

(4) P. Fitton and J. E. McKeon, *Chem. Commun.*, 4 (1968).

(5) M. Herberhold, *Angew. Chem. Intern. Ed. Engl.*, **7**, 305 (1968).

(6) M. Rosenblum, R. W. Fish, and C. Bennet, *J. Am. Chem. Soc.*, **86**, 5166 (1964).

(7) R. L. Brandon, J. H. Osiecki, and A. Ottenberg, *J. Org. Chem.*, **31**, 1214 (1966).

(8) J. W. Fitch and J. J. Lagowski, *Inorg. Chem.*, **4**, 864 (1965).

(9) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

(10) E. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *J. Am. Chem. Soc.*, **89**, 4540 (1967).

(10a) NOTE ADDED IN PROOF.—The crystal structure of $[Pt((C_6H_5)_3P)_2 \cdot TCNE]$ has also been reported by C. Panattoni, G. Bombieri, U. Belluco, and W. H. Baddley, *ibid.*, **90**, 798 (1968). The details of the Pt–TCNE bonding appear similar to the iridium complex.

(11) D. A. Bekoe and K. N. Trueblood, *Z. Krist.*, **113**, 1 (1960).

(12) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. II, Methuen & Co., London, 1968, pp 2–6.

(13) O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).

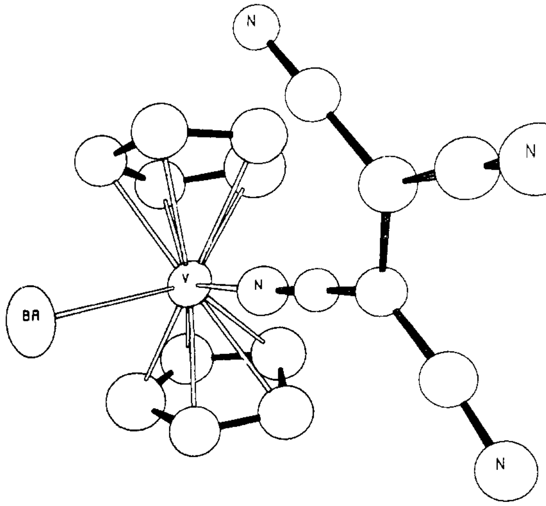

Figure 1.—Molecular structure of $(\pi\text{-}C_5H_5)_2VBr\cdot TCNE$.

We report here the preparation, properties, and preliminary crystal structure of $(\pi\text{-}C_5H_5)_2VBr\cdot TCNE$. As expected, the results clearly indicate that the vanadium has been oxidized by TCNE and that the TCNE moiety is attached to vanadium rather than to a cyclopentadienyl ring, as in the π-charge-transfer complexes. However, the TCNE is σ bonded to vanadium through a nitrile nitrogen, in contrast to the "π-bonded" TCNE moiety observed in the iridium structure[9] I. The oxidation state of TCNE is discussed on the basis of vibrational spectra, and the contrast in metal–TCNE bond types is discussed.

Experimental Section

All operations were conducted in a Vacuum Atmospheres inert-atmosphere box under an atmosphere of nitrogen. The atmospheric purity was such that an exposed 25-W light bulb would burn for 1 or 2 weeks in the box. Solvents were reagent grade and were deoxygenated by bubbling prepurified nitrogen through them for at least 1 hr. Tetrahydrofuran was distilled from CaH_2 under nitrogen before use. Eastman TCNE was not badly discolored and was used as received. Infrared spectra were measured as Nujol mulls or pellets (NaCl, KBr, CsI) or were measured in THF solution on a Perkin-Elmer 621. Conductance measurements were done with an Industrial Instruments Model RC 16B bridge at 25°. Magnetic susceptibilities were done by the Gouy method. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

Preparation of Complexes.—**$(\pi\text{-}C_5H_5)_2VCl\cdot TCNE$.**—A 0.65-g sample of $(\pi\text{-}C_5H_5)_2VCl$ (3.0 mmol, obtained from vanadocene and excess CH_2Cl_2 in hexane) was dissolved in 20 ml of THF. A solution of 0.39 g of TCNE (3.0 mmol) in 5 ml of THF was added dropwise, with stirring, to the $(C_5H_5)_2VCl$ solution over a period of 2 min. The solution immediately turned green, and gold crystals began depositing. The mixture was allowed to stand for 30 min and was filtered, washed twice with 20 ml of hexane, and sucked dry. This gave 0.75 g (72%) of gold microcrystalline products. *Anal.* Calcd for $(\pi\text{-}C_5H_5)_2VCl\cdot TCNE$: C, 55.75; H, 2.90; N, 16.25; Cl, 10.30. Found: C, 55.52; H, 3.00; N, 16.49; Cl, 10.20.

$(\pi\text{-}C_5H_5)_2VBr\cdot TCNE$.—Excess CH_2Br_2 in a few milliliters of hexane was added to 1.10 g of vanadocene (0.0061 mol) dissolved in 30 ml of hexane. There was an immediate reaction, and blue, flocculent $(\pi\text{-}C_5H_5)_2VBr$ appeared. This was filtered, washed with hexane, and sucked dry. All of the $(\pi\text{-}C_5H_5)_2VBr$ so obtained was redissolved in a minimum of THF, and 0.78 g of TCNE (0.0061 mol) in a few milliliters of THF was added. In a few minutes gold, microcrystalline $(\pi\text{-}C_5H_5)_2VBr\cdot TCNE$ was filtered, washed with THF and hexane, and sucked dry. The yield was 80% based on vanadocene. *Anal.* Calcd for $(\pi\text{-}C_5H_5)_2VBr\cdot TCNE$: C, 49.32; H, 2.59. Found: C, 49.60; H, 2.58.

$(\pi\text{-}C_5H_5)_2VI\cdot TCNE$.—About 1 ml of *n*-propyl iodide was added to a solution of 0.54 g of vanadocene (0.0030 mol) in 40 ml of hexane. Green, flocculent $(\pi\text{-}C_5H_5)_2VI$ precipitated immediately and was filtered and washed with hexane. All of the product was then dissolved in 40 ml of THF to give a green-blue solution. A 0.40-g sample of TCNE (0.0031 mol) in 20 ml of THF was then added and the solution immediately became green. After 5 min 60 ml of hexane was slowly added, and gold microcrystals appeared. These were filtered and washed with hexane. The yield was 33%. *Anal.* Calcd for $(\pi\text{-}C_5H_5)_2VI\cdot TCNE$: C, 44.01; H, 2.31. Found: C, 44.20; H, 2.36.

Each of the TCNE complexes occurs as gold microcrystals. Solubilities are slight in common organic solvents, and green solutions are obtained. The complexes are insoluble in water. On exposure to air, the crystals blacken in 30 min. The green solutions in THF or CH_2Cl_2 turn red on exposure to atmospheric oxygen. On long standing (overnight) in the absence of air, the green solutions become an intensely deep purple with deposition of some insoluble matter. The solid adducts are diamagnetic and are nonconductors in nitrobenzene just after dissolving, but rapid dissociation to ionic products was observed. The complexes decompose at *ca.* 150° on heating.

KTCNE.—This was prepared from KCN and TCNE in acetonitrile, according to the published method.[13]

Na_2TCNE.—This was prepared from NaH and tetracyanoethane, followed by removal of the solvating glyme, according to the published method.[13]

X-Ray Diffraction of $(\pi\text{-}C_5H_5)_2VBr\cdot TCNE$.—A small gold platelet (0.25 mm along the crystal *a* axis, 0.05 mm along *b*, and 0.25 mm along *c*, with errors of ±0.02 mm in each dimension) of $(\pi\text{-}C_5H_5)_2VBr\cdot TCNE$ was sealed in a 0.30-mm diameter borosilicate glass capillary with a wall thickness of 0.01 mm. In spite of this precaution there was considerable surface decomposition leading to a black crystal (*vide supra*) after several weeks. This did not, however, seem to affect the crystallinity of the sample, and a zero-layer Weissenberg photograph taken after all of the data had been collected indicated that there was no change in diffracted intensities during data collection.

On the basis of Weissenberg (Cu $K\bar{\alpha}$; λ 1.5418 Å) and precession photographs (Mo $K\bar{\alpha}$; λ 0.717 Å) we were able to determine the parameters of the orthorhombic cell as a_0 = 21.09 (4) Å, b_0 = 11.68 (2) Å, and c_0 = 12.79 (2) Å. Systematic absences observed for $0kl$ with $l = 2n + 1$, $h0l$ with $l = 2n + 1$, and $hk0$ with $h + k = 2n + 1$ uniquely suggested the space group to be Pccn. The density of the crystal, 1.64 (3) g/cm^3, measured by flotation in CCl_4–C_6H_5I, indicated 8.01 formula units of the adduct per cell, requiring no molecular symmetry.

Reflections were collected on a Nonius integrating Weissenberg camera for layers *hk*0 through *hk*6 to sin θ = 0.86 (nickel-filtered Cu $K\bar{\alpha}$ radiation) using a multiple-film technique. The intensities of the elongated spots were estimated by visual comparison with a calibrated set of timed exposures, with only 577 of the 1423 accessible reflections being measurable above background. The data were corrected for Lorentz and polarization effects and spot shape but not for absorption (μ = 90.0 cm^{-1} and the transmission factor varies from 0.2 to 0.5), and the data from different layers were scaled individually during refinement. The structure was solved using the heavy-atom method.

All calculations were performed on an IBM 360-50 computer. The Fourier program was Zalkin's FORDAP[14] and full-matrix least-squares refinement was done with Busing, Martin, and Levy's ORFLS.[15] The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized

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[14] A. Zalkin, Lawrence Radiation Laboratory, Berkeley, Calif., unpublished data.

[15] W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES ($\times$2.7 ELECTRONS) FOR $V(C_5H_5)_2Br\cdot TCNE$

H	K	FOBS	H	K	FOBS	H	K	FOBS	H	K	FOBS	H	K	FOBS	H	K	FOBS	H	K	FOBS	H	K	FOBS	H	K	FOBS	H	K	FOBS
****	L=	0 **	5	7	170	10	3	243	1	10	206	6	3	52	7	9	137	2	6	112	7	3	212	5	1	247	0	2	289
4	0	466	7	7	37	12	3	185	3	10	184	8	3	110	8	9	96	3	6	104	8	3	87	6	1	111	2	2	108
6	0	333	9	7	89	14	3	162	9	10	117	9	3	202	9	9	182	7	6	180	9	3	260	7	1	132	4	2	247
8	0	188	11	7	78	16	3	229	11	10	126	10	3	78	10	9	96	1	7	124	10	3	88	8	1	206	6	2	199
10	0	457	15	7	75	18	3	142	4	11	68	11	3	57	6	10	88	2	7	215	13	3	212	9	1	128	7	2	162
12	0	297	17	7	55	20	3	88	5	11	67	12	3	87	2	11	115	3	7	126	15	3	100	10	1	103	9	2	139
14	0	53	19	7	73	21	3	78	1	12	162	13	3	189	3	11	96	4	7	242	0	4	170	1	2	115	10	2	71
16	0	200	0	8	130	1	4	71	****	L=	2 **	15	3	156	7	11	123	7	7	94	1	4	87	3	2	97	11	2	118
18	0	106	2	8	119	2	4	203	3	0	215	0	4	242	9	11	143	12	7	137	2	4	74	4	2	78	13	2	118
3	1	572	4	8	350	3	4	67	4	0	81	1	4	164	0	12	131	14	7	139	3	4	91	5	2	234	15	2	115
5	1	378	6	8	208	5	4	527	5	0	92	2	4	271	****	L=	3 **	1	8	178	4	4	223	7	2	167	16	2	106
7	1	28	8	8	54	6	4	63	6	0	428	4	4	540	1	1	580	7	8	91	5	4	118	8	2	94	17	2	107
9	1	143	12	8	68	7	4	294	7	0	220	5	4	154	3	1	178	2	9	133	6	4	241	11	2	103	0	3	93
13	1	132	7	9	96	10	4	70	8	0	209	6	4	342	4	1	102	1	10	151	7	4	230	1	3	276	1	3	181
15	1	73	9	9	298	11	4	87	9	0	253	7	4	94	5	1	394	1	12	155	9	4	141	2	3	140	2	3	49
19	1	43	11	9	75	15	4	135	10	0	357	8	4	119	6	1	278	2	12	141	11	4	169	3	3	270	3	3	322
0	2	799	0	10	81	17	4	129	11	0	188	11	4	137	7	1	177	****	L=	4 **	13	4	105	5	3	176	7	3	110
2	2	749	2	10	89	21	4	100	12	0	314	13	4	96	8	1	423	2	0	245	0	5	144	7	3	104	9	3	111
4	2	721	1	11	98	2	5	339	13	0	113	16	4	104	9	1	100	3	0	191	2	5	84	1	4	258	10	3	169
6	2	277	3	11	62	3	5	76	15	0	87	0	5	67	10	1	167	4	0	89	3	5	176	3	4	106	11	3	112
8	2	166	7	11	105	4	5	265	16	0	156	1	5	188	11	1	148	5	0	273	4	5	173	4	4	120	13	3	121
10	2	303	9	11	123	5	5	125	17	0	147	2	5	107	1	2	440	6	0	128	5	5	83	5	4	106	0	4	154
12	2	112	0	12	94	6	5	63	18	0	126	3	5	262	3	2	172	7	0	250	6	5	135	6	4	108	2	4	57
18	2	98	2	12	71	7	5	79	20	0	73	4	5	112	4	2	72	8	0	299	8	5	101	7	4	162	3	4	112
20	2	43	****	L=	1 **	8	5	108	2	1	41	5	5	88	5	2	201	9	0	99	10	5	68	1	5	246	4	4	61
1	3	385	2	1	470	9	5	94	3	1	150	6	5	91	6	2	145	10	0	263	13	5	109	2	5	299	5	4	109
3	3	593	4	1	385	10	5	172	4	1	263	7	5	78	7	2	202	11	0	204	0	6	192	3	5	188	6	4	87
5	3	82	5	1	104	12	5	298	5	1	222	8	5	68	11	2	241	12	0	190	3	6	105	4	5	160	7	4	82
7	3	105	6	1	616	14	5	201	7	1	225	9	5	93	12	2	95	13	0	220	4	6	277	5	5	138	9	4	142
9	3	136	7	1	133	16	5	98	9	1	152	11	5	101	1	3	402	14	0	133	5	6	100	6	5	108	10	4	75
11	3	75	8	1	498	18	5	82	10	1	60	13	5	155	2	3	82	15	0	116	6	6	270	7	5	134	11	4	140
13	3	334	9	1	62	2	6	84	11	1	158	15	5	136	3	3	272	1	1	200	7	6	116	1	6	110	13	4	86
15	3	167	10	1	390	3	6	265	12	1	90	1	6	131	5	3	275	2	1	132	8	6	68	2	6	100	16	4	128
19	3	62	11	1	173	5	6	404	13	1	125	2	6	110	6	3	83	3	1	277	9	6	144	1	7	142	0	5	97
0	4	309	12	1	280	6	6	53	0	2	635	3	6	190	7	3	81	5	1	105	10	6	96	2	7	144	1	5	93
2	4	607	14	1	92	7	6	191	1	2	184	4	6	360	8	3	148	7	1	66	14	6	70	3	7	133	2	5	86
4	4	336	16	1	195	8	6	107	2	2	567	6	6	414	9	3	171	9	1	101	0	7	164	4	7	162	3	5	151
6	4	209	18	1	284	9	6	77	3	2	54	8	6	88	10	3	238	10	1	75	2	7	126	5	7	164	4	5	117
8	4	174	20	1	186	15	6	56	4	2	353	9	6	131	11	3	92	11	1	87	4	7	155	****	L=	6 **	6	5	136
10	4	175	22	1	64	2	7	425	5	2	135	10	6	103	12	3	106	0	2	434	6	7	111	2	0	144	7	5	141
12	4	69	1	2	559	3	7	95	7	2	255	0	7	146	16	3	148	1	2	309	8	7	127	3	0	59	9	5	104
20	4	79	3	2	331	4	7	298	8	2	232	2	7	134	1	4	178	2	2	414	11	7	102	4	0	285	0	6	149
22	4	65	4	2	139	5	7	90	9	2	70	6	7	69	3	4	82	3	2	76	0	8	104	5	0	137	4	6	108
1	5	372	5	2	285	7	7	49	10	2	283	7	7	85	5	4	403	6	2	112	4	8	167	6	0	230	5	6	119
3	5	253	6	2	281	10	7	84	11	2	114	8	7	87	6	4	84	7	2	188	6	8	130	7	0	165	6	6	94
5	5	46	7	2	275	12	7	182	12	2	110	9	7	107	7	4	260	8	2	89	9	8	112	8	0	94	7	6	90
7	5	120	8	2	132	14	7	186	13	2	116	10	7	83	10	4	94	9	2	137	2	9	146	9	0	101	10	6	113
9	5	59	9	2	77	16	7	107	15	2	106	11	7	122	11	4	116	10	2	175	3	9	111	11	0	165	11	6	115
11	5	147	11	2	177	1	8	250	16	2	101	0	8	111	1	5	170	12	2	65	4	9	161	13	0	183	12	6	106
13	5	146	13	2	74	3	8	211	17	2	113	2	8	102	2	5	281	13	2	130	7	9	163	15	0	124	13	6	89
15	5	192	15	2	198	7	8	70	18	2	105	4	8	233	3	5	248	15	2	108	9	9	104	16	0	127	0	7	95
0	6	63	17	2	88	9	8	125	19	2	80	6	8	229	4	5	216	0	3	88	2	11	102	17	0	140	2	7	126
2	6	194	2	3	119	11	8	117	0	3	260	7	8	99	5	5	203	1	3	168	3	11	122	2	1	98	4	7	91
4	6	484	3	3	165	12	8	57	1	3	71	8	8	111	6	5	133	2	3	137	****	L=	5 **	3	1	165	0	8	160
6	6	645	4	3	208	13	8	82	2	3	56	10	8	79	7	5	181	3	3	306	1	1	582	5	1	82	4	8	106
10	6	198	5	3	353	2	9	122	3	3	64	0	9	91	12	5	152	4	3	43	2	1	431	6	1	62	6	8	87
16	6	62	6	3	327	4	9	124	4	3	164	2	9	121	14	5	176	5	3	130	3	1	248	9	1	112	2	9	128
20	6	80	8	3	401	11	9	75	5	3	218	3	9	77	1	6	92	6	3	85	4	1	91	13	1	88	7	9	149
3	7	55	9	3	82	12	9	98																					

and in the last five cycles of refinement the weights (w) were: $w = [1.0 + (F_o/20.0) + (F_o^2/4800)]^{-1}$.

The atomic scattering powers of bromine and vanadium were corrected for the real and imaginary parts of the anomalous dispersion correction.[16] The atomic scattering powers of Br^-, V^+, and neutral nitrogen and carbon atoms were taken from standard tables.[17]

At the present stage of refinement $R = 0.13$ and $wR = 0.17$. We feel that the structure has been refined to the limit justified by the quality of our data. However, since distances between light atoms have standard deviations typically of 0.08 Å, we present no atom coordinates or derived distances. The observed structure factors are listed in Table I.

Discussion

Infrared Spectra and Molecular Structure.—The infrared spectra of the three adducts are identical from 4000 to 300 cm^{-1}, and identical spectra are obtained in Nujol mulls, thin films from evaporated CH_2Cl_2 solutions, alkali halide pellets (NaCl, KBr, CsI), and CH_2Cl_2, tetrahydrofuran, and nitrobenzene solutions (the nitrobenzene solutions are unstable). These results suggest that each of the adducts has the same molecular structure and that this structure is preserved in solution. The X-ray molecular structure of the bromide adduct is shown in Figure 1. $(C_5H_5)_2VCl\cdot TCNE$ has infrared absorptions (in cm^{-1}) at 3100 (m), 2211 (w), 2192 (s), 2152 (s), 2128 (s), 1437 (sh), 1425 (m), 1397 (m), 1292 (w), 1192 (w), 1120 (w), 1058 (w), 1019 (m), 1005 (m), 950 (w), 830 (s), 509 (m), 280 (m), and 250 (m) (Figure 2). All of the peaks with the exception of those at 2100–2200 cm^{-1} and those below 600 cm^{-1} are clearly characteristic of π-bonded C_5H_5, nearly every vibration having its counterpart in spectra which we obtained of $(C_5H_5)_2VCl$ and $(C_5H_5)_2TiCl_2$ (see Figure 2). The bromide and iodide adducts have ir spectra nearly identical with $(C_5H_5)_2VCl\cdot TCNE$, the only exceptions being that these latter complexes exhibit a *single* vibration between 200 and 250 cm^{-1} in $(C_5H_5)_2VCl\cdot TCNE$. In CsI pellets, these medium-intensity single vibrations occur at 277 and 275 cm^{-1} for $(C_5H_5)_2VI\cdot TCNE$ and $(C_5H_5)_2VBr\cdot TCNE$, respectively. We assign one of the low-frequency modes in the chloride adduct to the V–Cl stretch. This assignment is consistent with the occurrence of a strong vibration at 257 cm^{-1} in $(C_5H_5)_2VCl$, which is absent in our spectra of $(C_5H_5)_2VBr$ and $(C_5H_5)_2VI$. The V–Br and V–I vibrations occur at frequencies too low to measure with our present instrumentation.

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(16) D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 214, Table 3.3.2.B.

(17) J. A. Ibers, ref 16, p 202, Table 3.3.1.A.

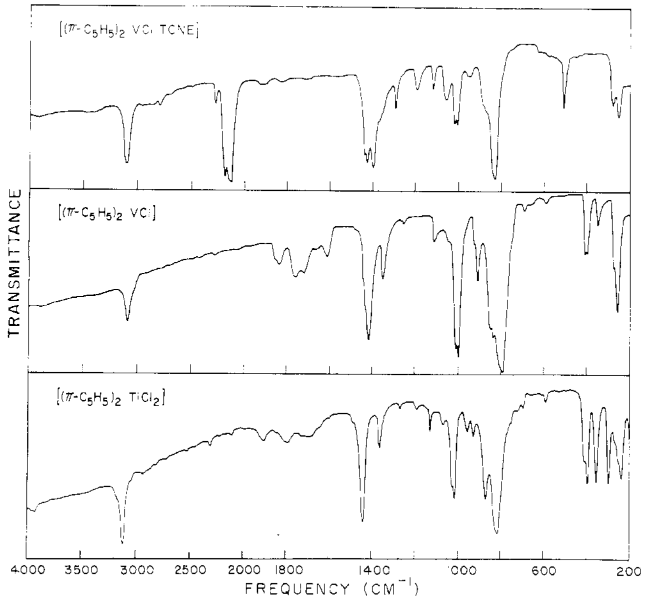

Figure 2.—Infrared spectra of various compounds in KBr pellets.

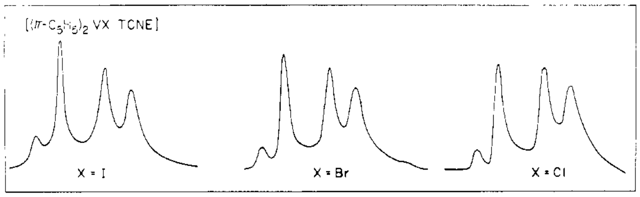

Figure 3.—Infrared spectra (absorbance scale) of the TCNE adducts in the triple-bond region. For a given adduct from left to right the vibrational frequencies are 2211, 2192, 2152, and 2128 cm^{-1} (±3 cm^{-1}). The four frequencies are identical within experimental error for each adduct.

Each of the adducts exhibits three strong vibrations and one weak vibration in the region 2125–2215 cm^{-1}, all of which are assigned to C≡N vibrations (the respective frequencies for all of the adducts are the same within experimental error). This result is most unusual, since in all previously known TCNE complexes either a *single* vibration near 2220 cm^{-1} is found,[1–5] or, for the ferrocene charge-transfer adduct, the C≡N absorptions appear as a doublet unchanged from free TCNE (2260 and 2225 cm^{-1}).[6] The multiplicity of C≡N vibrations is consistent with the effective (local) C_s symmetry of the coordinated TCNE, as in Figure 1. In Figure 3 we show the four C≡N vibrations for each adduct on an expanded scale. Referring again to Figure 1 and considering the cyclopentadienyl rings as point ligands, the vanadium coordination may be described as distorted tetrahedral with one of the coordination positions occupied by an N-bonded TCNE group.

The TCNE Group.—The coordinated TCNE group exhibits four very low-frequency C≡N vibrations. In order to understand better the ir results, we have carried out CNDO/2 calculations on TCNE, TCNE$^-$, and TCNE^{2-}, using the standard carbon and nitrogen parameters.[18] According to these results the additional electron density enters a π MO which is antibonding with respect to each of the C≡N bonds and also with respect to the central C=C bond. One therefore expects a significant lowering of $\nu_{C\equiv N}$ and $\nu_{C=C}$, if the TCNE acts as an electron acceptor. Some of the experimental and calculated results are in Tables II and III. According to Table II, the calculated C—C π-bond order parallels the observed $\nu_{C=C}$. We assign the new vibration at 1400 cm^{-1} in the spectra of (π-C_5H_5)$_2$VX·TCNE to the central C=C stretch in coordinated TCNE (see Figure 2). This frequency is quite low and is nearly what one expects for coordinated TCNE$^-$, according to Table II. The same thing is apparent in the C≡N frequencies in Table III. The TCNE adducts show C≡N vibrations at quite low frequencies, near what is found for TCNE$^-$ and TCNE^{2-}. Finally, the central C=C bond in the coordinated TCNE group is longer than its counterpart in free TCNE (although not significantly so at this stage of refinement), lending further support to the idea that the TCNE has been reduced and is coordinated to vanadium as TCNE$^-$. A slight shortening of the external C—C bond lengths and lengthening of the central C=C and the C≡N's would be anticipated on the basis of our MO and ir results, but the present stage of refinement of this structure does not permit a direct confir-

Table II

Bond Orders, Bond Lengths, and Vibration Frequencies for TCNE and Related Species

	Central C—C bond length, Å	Central C=C π-bond order (CNDO or extrapolated)	C=C str, cm^{-1} [e]
TCNE	1.339[a]	0.86	1570
TCNE$^-$	(1.41)[b]	0.48	1370
TCNE^{2-}	(1.45)[b]	0.12	1260
"N" bonded TCNE	(1.40)[b]	~0.54[c]	1400–1425
"Olefin" bonded TCNE	1.507 (15)[d]	...	...

[a] Reference 9. The value 1.339 Å for TCNE was given in ref 9 as the result of a private communication with D. A. Bekoe and K. N. Trueblood. However, the published value[11] is 1.317 (9) Å. [b] From a plot of C—C bond order *vs.* bond length, normalized so that C=C in TCNE is 1.34 Å: C. A. Coulson, "Valence," 2nd ed, Oxford University Press, London, 1961, p 270, Figure 9.16. [c] This C—C bond order was extrapolated from a plot of calculated (CNDO) bond orders *vs.* observed ν_{CC}. The TCNE, TCNE$^-$, and TCNE^{2-} bond orders are the calculated results. [d] Reference 9. [e] This work.

Table III

C≡N Stretching Frequencies for Various TCNE Compounds (cm^{-1})

Compound	Band I	II	III	IV
IrBr(CO)(P(C_6H_5)$_3$)$_2$TCNE[a]	2230	...	...	...
Pt((C_6H_5)$_3$P)$_2$TCNE[b]	2230	...	...	...
TCNE[c]	2260	2225	...	...
TCNE$^-$ [c]	2200	2175	...	...
TCNE^{2-} [c]	2160	2095	...	...
(π-C_5H_5)$_2$VX·TCNE[d]	2211	2192	2152	2128

[a] Reference 1. [b] Reference 3. [c] This work. Alkali halide pellets. [d] The frequencies are independent of X to ±3 cm^{-1}.

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(18) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, 5136 (1965).

mation. The low values for the $C\equiv N$ and $C=C$ stretching vibrations leave little doubt as to the extent of weakening of the $C\equiv N$ and $C=C$ bonds, however.

Interaction of Coordinated Bromide and Coordinated TCNE$^-$.—The packing of the groups around vanadium is quite crowded as evidenced by four short bromine to cyclopentadienide carbon distances of 3.1–3.2 Å and a bromine to coordinated nitrogen contact of 3.1–3.2 Å. These contacts are all well inside the sum of the van der Waals radii (3.7 and 3.5 Å, respectively) and while they explain the long V–Br distance (2.59 (1) Å, 0.25 Å longer than expected) the most important consequence is expected to be a possible direct interaction between bromine and the electron-accepting TCNE group. Considering now Figure 3, we note that the relative intensities of the first, third, and fourth $C\equiv N$ vibrations are constant as X is varied but that the relative intensity of the second highest frequency vibration increases significantly in the order $Cl < Br < I$. This result suggests that the second highest vibrational frequency (Figure 3) is primarily due to $C\equiv N$—V stretching and that its intensity is markedly affected by the adjacent halogen. In line with what is expected for an "electron-demanding" $C\equiv N$ stretch, the intensity is enhanced when a highly polarizable I^- is adjacent to the $C\equiv N$ oscillator. In further support of such an interaction, we observe that there is no obvious reason for the particular orientation assumed by the coordinated TCNE. Thus the TCNE moiety is oriented perfectly for acceptance of halide electron density into the π^* orbital. On steric grounds the TCNE could lie *in* the Br–V–N plane rather than perpendicular to that plane—there are no obvious interferences, either intra- or intermolecular. We therefore conclude that this intramolecular interaction plays some part in determining the molecular geometry. It is of interest to note that Br^- does form an intensely red-orange complex with TCNE, whose thermodynamic properties have been measured.[19] We have so far been unable to *crystallize* such a complex, however.

Summary and Conclusions

All of the evidence presented is consistent with coordination of TCNE$^-$ to vanadium by means of one of the nitrile nitrogens. This contrasts with the only other reported[10a] X-ray structure in which TCNE is bound to a metal, namely, $IrBr(CO)((C_6H_5)_3P)_2TCNE$,[9] where "$\pi$-olefin" coordination is observed. The structure observed here suggests that the reason for the strong infrared-active $C=C$ stretch in NaTCNE and Na_2TCNE lies in nitrile coordination to the alkali metal counterion. This "anomalous" infrared activity was earlier ascribed to vibronic effects in NaTCNE and KTCNE.[20] Such coordination to alkali metal counterions is also observed in alkali metal salts of the tetracyanoquinodimethanide anion[21] and in the sodium tricyanomethanide ion, $Na[C(CN)_3]$.[22a] We further observe that infrared results suggest that the tricyanomethanide ion bonds to metal cabonyl moieties by N-donation from one of its nitrile nitrogens, as in $(C_2H_5)_4N[Cr(CO)_5NCC(CN)_2]$, for example.[22b]

It is quite useful to classify the known complexes of TCNE according to the hard and soft acid–base scheme.[23] All previous complexes of TCNE which involve a metal–TCNE bond[1–5] may be regarded as soft–soft interactions, where the soft metal complex donates its d electrons to the soft π-acceptor TCNE. Thus the *metal complex acts as the soft base* and *TCNE is the soft acid*. Such behavior is expected for metals in low oxidation states (Ir(I), Pt(0), etc.) with soft ligands ($(C_6H_5)_3P$, CO, etc), as has been observed.[1–5] This *basic* behavior is also exhibited by certain metal complexes in their reactions with acids (BF_3, BCl_3, BH_3, $Al(CH_3)_3$, etc.).[24] In contrast, the present series of TCNE complexes may be regarded as a hard–hard interaction, where the *hard* $(\pi\text{-}C_5H_5)_2V^{IV}X^+$ *group accepts* electron density from the relatively *hard σ-donor nitrile nitrogen of TCNE$^-$*. Thus, the metal complex is the hard acid and TCNE$^-$ is the hard base. This behavior is quite consistent with expectations based on Burmeister's results for $(\pi\text{-}C_5H_5)_2Ti^{IV}X_2$ (X is a pseudohalide or halide).[25] Those results[25] are best explained if one assumes that the $(\pi\text{-}C_5H_5)_2Ti^{IV}$ moiety (and therefore presumably the $(\pi\text{-}C_5H_5)_2V^{IV}$ moiety) behaves as a hard acid. Although σ donation of electron density appears to be important in the vanadium–TCNE bonding, we emphasize that the diamagnetism of the complexes suggests significant $d\pi$–$p\pi$ interaction. Thus, in our view, the complexes are best regarded (formally) as V(IV) interacting with TCNE$^-$. Since V(IV) is a d^1 ion and TCNE$^-$ is a π radical, we might have expected the two spins to be uncoupled or only weakly coupled. However, the observed diamagnetism implies a strong interaction of the single "vanadium" electron with the π-electron density on TCNE$^-$.

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