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The Cesium Tetracyanoethylenide Radical Salt†

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Tetracyanoethylene (TCNE) reacts in aprotic dimethoxyethane solution with a cesium metal mirror to yield black crystals of $[TCNE^{\bullet-}Cs^+]^{\bullet}_{\infty}$. The solvent-free radical salt C_6N_4Cs crystallizes in the monoclinic system $P2_1/n$ with $Z = 8$, fw 261.0, $a = 858.39$ (40) pm, $b = 1762.76$ (90) pm, $c = 1030.49$ (50) pm, and $\beta = 93.43$ (4)°; $R_w = 3.6\%$. It contains staples of two differently structured $TCNE^{\bullet-}$ radical anions with two different cesium countercations, which are coordinated to eight and nine nitrogens. The crystal structure is compared to those of the respective sodium and potassium salts as well as to cesium pentacyanopropenide and cesium tetracyanoquinodimethanide.

Introduction

The electron-acceptor molecule tetracyanoethylene, characterized by a multitude of data,[1-3] is considered to be a prototype charge-transfer complex ligand[4] and is of actual interest as a counteranion in organic conductors and ferromagnets.[1] We have selected the $TCNE^{\bullet-}$ radical anion to study the influence of countercations of different sizes and, therefore, of different solvations[5] (Figure 1) by the energetically favorable chelating ligand dimethoxyethane (DME) in radical salts such as $[TCNE^{\bullet-}(K^+DME)]^{\bullet}_{\infty}$[3] or $[TCNE^{\bullet-}(Na^+DME)]^{\bullet}_{\infty}$.[6]

In general, the crystallization of alkali metal organic compounds[8] is influenced by several competing effects, among which solvatation can play a dominant role. The hydration enthalpies of the group I cations, for instance, double from only 10-fold hydrated Cs^+ to $[Li^+(H_2O)_{25}]^+$, in which according to transference measurements the rather small cation Li^+ is surrounded by three layers of altogether 25 water molecules[7] (Figure 1a). The differences in solvation of alkali metal cations depend largely on their ionic radii, which may be correlated with effective nuclear charges as defined according to Slater[9] by their first atomic ionization energies (Figure 1b).

Cs atoms with their rather low ionization energy of only 3.89 eV, as well as Cs^+ cations with the largest ionic radius of 169 pm among the nondecaying group I elements, are one extreme end of the line. Compared with the many of structures of organic lithium derivatives known,[10] only few have been reported for cesium compounds. We succeeded in growing black single crystals of the air- and moisture-sensitive title radical salt and determining its structure in a 150 K nitrogen flow.[11]

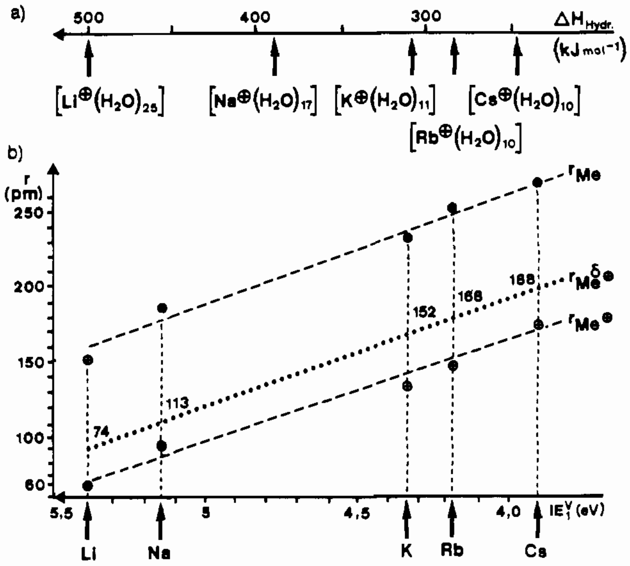

Figure 1. (a) Hydration enthalpies of the differently hydrated alkali metal cations.[7] (b) Correlation of atomic (r_{Met}) and ionic radii (r_{Met^+}) with the first vertical ionization energies of alkali metal atoms. (Numbers given are for 80% ionic character.[8])

Experimental Section

Preparation and Single-Crystal Growth of $[TCNE^{\bullet-}Cs^+]^{\bullet}_{\infty}$. In a Schlenk trap, carefully heated at 10^{-2} mbar to remove as much as possible of the surface chemisorbed water, a sealed ampule containing approximately 5 g (38 mmol) of cesium metal (Chemetall, Frankfurt) is placed; the metal is melted at about 50 °C and the seal broken under especially purified Ar. By shaking of the trap, a Cs metal mirror is generated at the wall of its lower third. *Caution*: *Cs metal can burn in air*! Under purified Ar, 30 mL of dimethoxyethane, twice distilled over Na/K alloy and degassed by repeated solidification and evacuation to 10^{-4} mbar, is added as well as 650 mg (5.1 mmol) of tetracyanoethylene, repeatedly recrystallized from 1,1-dichloroethane and sublimed at 10^{-4} mbar. After

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† Structures of Charge-Perturbed or Sterically Overcrowded Molecules. 16. For part 15, see ref 6.

(1) Miller, S. J.; Calabrese, J. C.; Rommelmann, H.; Chittipedi, S. R.; Zhang, J. H.; Reiff, W. M.; Epstein, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 769 and references therein.

(2) Dixon, D. A.; Miller, J. S. *J. Am. Chem. Soc.* **1987**, *109*, 3656 and references therein.

(3) Bock, H.; Ruppert, K.; Fenske, D.; Goesmann, H. *Z. Anorg. Allg. Chem.* **1991**, *595*, 275 and references therein.

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(5) For a review cf.: Bock, H.; Ruppert, K.; Näther, C.; Havlas, Z.; Herrmann, H.-F.; Arad, C.; Göbel, I.; John, A.; Meuret, J.; Nick, S.; Rauschenbach, A.; Seitz, W.; Vaupel, T.; Solouki, B. *Angew. Chem.* **1992**, *104*, 564; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 550 and references therein.

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(7) Wiberg, N. *Hollemann-Wiberg, Lehrbuch der Anorganischen Chemie*, Edition 91.-100., de Gruyter: Berlin, 1985; p 954.

(8) Cf. the review by: Schade, C.; Schleyer, P. v. R. Sodium, Potassium, Rubidium, and Caesium: X-Ray Structural Analysis of their Organic Compounds. *Adv. Organomet. Chem.* **1987**, *27*, 169 and references therein.

(9) Slater, J. C. *Phys. Rev.* **1930**, *36*, 57. Cf.: Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; Saunders: Philadelphia, PA, 1977; p 44f.

(10) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353 and references therein. Cf. also: Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47.

(11) Ruppert, K. Ph.D. Thesis, University of Frankfurt, 1992.

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Table I. Crystallographic Data for [TCNE$^{\bullet-}$Cs$^+$]

chem formula C_6N_4Cs	space group $P2_1/n$ (No. 14)
fw 261	$T = 150$ K
$a = 8.584$ (4) Å	$\lambda = 0.710\ 73$ Å
$b = 17.628$ (9) Å	$\rho_{calcd} = 2.23$ g cm^{-3}
$c = 10.305$ (5) Å	μ(Mo Kα) = 4.66 mm^{-1}
$\beta = 93.43$ (4)	$R^a = 0.031$
$V = 1556.47$ Å^3	$R_w{}^b = 0.036$
$Z = 8$	

[a] $R = \sum[F_o - F_c]/\sum F_o$. [b] $R_w = \sum[F_o - F_c]w^{1/2}/\sum F_o w^{1/2}$.

Table II. Fractional Atomic Coordinates and Thermal Parameters for [TCNE$^{\bullet-}$Cs$^+$]

	x	y	z	U(eq), Å^2
Cs(1)	1777 (1)	4777 (1)	1714 (1)	20 (1)
Cs(2)	−3110 (1)	4448 (1)	3877 (1)	21 (1)
C(1)	2717 (5)	7755 (3)	−316 (4)	21 (1)
C(2)	4108 (5)	7789 (3)	−972 (5)	22 (1)
C(3)	4835 (5)	7107 (3)	−1379 (5)	26 (1)
C(4)	4906 (5)	8493 (3)	−1086 (4)	23 (1)
C(5)	2120 (4)	8441 (3)	219 (4)	18 (1)
C(6)	2072 (5)	7056 (3)	65 (4)	23 (1)
N(1)	5350 (5)	6538 (3)	−1679 (5)	33 (1)
N(2)	5487 (5)	9081 (3)	−1140 (4)	33 (1)
N(3)	1732 (4)	9020 (2)	583 (4)	24 (1)
N(4)	1611 (5)	6470 (3)	334 (5)	33 (1)
C(10)	7695 (5)	1789 (3)	3355 (4)	20 (1)
C(11)	9088 (5)	1971 (3)	2686 (4)	22 (1)
C(12)	6982 (5)	2331 (3)	4123 (5)	22 (1)
C(13)	7225 (5)	1032 (3)	3466 (4)	21 (1)
C(14)	9581 (5)	2728 (3)	2672 (4)	23 (1)
C(15)	10000 (5)	1377 (3)	2236 (4)	21 (1)
N(10)	6844 (5)	407 (3)	3552 (4)	25 (1)
N(20)	6393 (5)	2775 (3)	4766 (5)	33 (1)
N(30)	10633 (4)	844 (2)	1880 (4)	25 (1)
N(40)	9886 (5)	3369 (3)	2705 (4)	28 (1)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	21 (1)	19 (1)	19 (1)	1 (1)	2 (1)	1 (1)
Cs(2)	23 (1)	19 (1)	23 (1)	1 (1)	3 (1)	1 (1)
C(1)	21 (2)	20 (2)	23 (2)	0 (2)	0 (1)	1 (2)
C(2)	18 (2)	20 (2)	29 (2)	5 (2)	0 (1)	−5 (2)
C(3)	22 (2)	33 (3)	23 (2)	7 (2)	0 (1)	−9 (2)
C(4)	21 (2)	32 (3)	17 (2)	−5 (2)	1 (1)	0 (2)
C(5)	17 (2)	23 (2)	14 (2)	0 (1)	2 (1)	2 (1)
C(6)	25 (2)	25 (2)	19 (2)	3 (2)	−2 (1)	−1 (2)
N(1)	30 (2)	35 (2)	33 (2)	7 (2)	5 (2)	−8 (2)
N(2)	32 (2)	40 (3)	26 (2)	−9 (2)	4 (1)	1 (2)
N(3)	24 (2)	26 (2)	21 (2)	0 (1)	0 (1)	1 (1)
N(4)	38 (2)	23 (2)	37 (2)	−1 (2)	4 (2)	7 (2)
C(10)	22 (2)	22 (2)	16 (2)	1 (2)	2 (1)	2 (2)
C(11)	19 (2)	24 (2)	21 (2)	1 (2)	0 (1)	0 (2)
C(12)	19 (2)	23 (2)	25 (2)	−5 (2)	2 (1)	3 (2)
C(13)	24 (2)	28 (3)	12 (2)	4 (2)	3 (1)	−4 (2)
C(14)	20 (2)	33 (3)	17 (2)	0 (2)	3 (1)	1 (2)
C(15)	17 (2)	27 (2)	19 (2)	−5 (2)	−2 (1)	4 (2)
N(10)	31 (2)	20 (2)	25 (2)	−6 (2)	9 (1)	−1 (2)
N(20)	39 (2)	27 (2)	33 (2)	0 (2)	10 (2)	−9 (2)
N(30)	22 (2)	24 (2)	29 (2)	5 (1)	3 (1)	1 (1)
N(40)	31 (2)	21 (2)	32 (2)	−4 (1)	0 (1)	−4 (2)

10 min, the solution turns black, and upon careful addition of five 2-mL layers of pure degassed *n*-hexane, black needles start to grow.

Collection and Refinement of X-ray Data. A single crystal of about 0.5-mm diameter was mounted under a continuous nitrogen flow at 150 K on a thin glass fiber. The data collection was carried out using an automated Siemens AED-II four-circle diffractometer employing Mo Kα radiation and a graphite monochromator. Intensity data were collected in the range $3 < 2\theta < 55°$ in the ω-scan mode. Of the 5947 reflections measured, 2666 were independent with $I > 2\sigma(I)$. The structure was solved by Patterson methods (SHELXTL-PLUS) followed by full-matrix least-squares refinement, which converged to final agreement factors of $R = 0.031$ and $R_w = 0.036$. After empirical absorption corrections, residuals of +1.35/−0.74 e/Å^3 near the Cs atoms were found. All atoms were anisotropically refined. Crystallographic data are summarized in Table I, atomic coordinates and thermal parameters in Table II, and selected bond lengths, angles, and contact distances in Table III.

Table III. Selected Bond Lengths (pm) and Angles (deg) for the Two Different TCNE$^{\bullet-}$ Species Coordinated by Eight (A) or Seven (B) Cs$^+$ Countercations[a] as Well as Contact Distances (pm) for Cs(1) and Cs(2)[b]

Cs(1)–Cs(2)	490.1 (3)	Cs(1)–N(4)	330.6 (5)
C(6)–N(4)	114.5 (7)	C(1)–C(2)	140.8 (6)
C(1)–C(5)	143.7 (6)	C(1)–C(6)	141.6 (7)
C(2)–C(3)	142.9 (7)	C(2)–C(4)	142.5 (7)
C(3)–N(1)	114.6 (7)	C(4)–N(2)	115.4 (7)
C(13)–N(10)	115.4 (6)	C(5)–N(3)	114.3 (6)
C(10)–C(11)	145.2 (6)	C(10)–C(12)	140.5 (6)
C(10)–C(13)	140.0 (7)	C(11)–C(14)	140.0 (7)
C(11)–C(15)	140.3 (6)	C(12)–N(20)	116.0 (7)
C(14)–N(40)	116.0 (7)	C(15)–N(30)	115.7 (6)

C(2)–C(1)–C(5)	118.7 (4)	C(2)–C(1)–C(6)	121.8 (4)
C(5)–C(1)–C(6)	118.2 (4)	C(1)–C(2)–C(3)	120.1 (4)
C(1)–C(2)–C(4)	120.2 (4)	C(3)–C(2)–C(4)	119.2 (4)
C(2)–C(3)–N(1)	176.2 (5)	C(2)–C(4)–N(2)	176.1 (5)
C(1)–C(5)–N(3)	174.2 (5)	C(1)–C(6)–N(4)	176.2 (5)
C(11)–C(10)–C(12)	121.0 (4)	C(11)–C(15)–N(30)	173.6 (5)
C(11)–C(10)–C(13)	119.9 (4)	C(12)–C(10)–C(13)	117.7 (4)
C(10)–C(11)–C(14)	118.3 (4)	C(10)–C(11)–C(15)	118.9 (4)
C(14)–C(11)–C(15)	122.2 (4)	C(10)–C(12)–N(20)	179.5 (5)
C(10)–C(13)–N(10)	179.6 (4)	C(11)–C(14)–N(40)	174.8 (5)

Cs(1): N(10b) = 330, N(2b) = 324, N(4) = 330, N(30c) = 319, N(3c) = 19, N(1a) = 339, N(10a) = 328, N(40d) = 316, Cs(2) = 490, Cs(1a) = 460, Cs(2a) = 482, Cs(2b) = 484

Cs(2): N(30b) = 334, N(3d) = 321, N(10b) = 326, N(2c) = 319, N(40a) = 348, N(20a) = 313, N(30c) = 338, N(1a) = 337, N(3b) = 327, Cs(1a) = 484, Cs(2a) = 454, Cs(1b) = 482, Cs(1) = 490

[a] Cf. Figure 7. [b] Cf. Figure 6.

AM 1 and MNDO Calculations. The semiempirical calculations[12] were performed by our group using the program versions SCAMP 4.1 (T. Clark, University of Erlangen) and MOPAC (QCPE No. 506) with an IBM RISC 6000/320H. They were either fully geometry-optimized or based on the experimentally determined structures. The parameters for sodium[13] were derived from experimental data for di- or triatomics.

Results and Discussion

Cs$^+$–DME Solvation. In contrast to the structure determinations of the other two group I tetracyanoethylenide radical anion salts prepared so far, $[(NC)_2C{=}C(CN)_2{}^{\bullet-}Met^+(H_3COCH_2CH_2OCH_3)]^{\bullet}_{\infty}$ with Met$^+$ = Na$^+$ [6] and K$^+$,[3] the structure determination of the Cs$^+$ salt proves much to our surprise that this compound does not contain any solvent molecules. Because the single crystals were grown under comparable conditions,[3,6] there must be some rationale for the crystallization of black C_6N_4Cs from the dimethyoxyethane/*n*-hexane solution (Experimental Section).

To begin with, dimethoxyethane (DME), due to its chelating properties, is an energetically favorable ligand for cation solvation. Its flexibility can be demonstrated by the respective average structure parameters determined for the other two TCNE$^{\bullet-}$ salts,[3,6] incorporated into an approximate correlation between the bite distance O···O and the dihedral angle ω(OC–CO) of DME (Figure 2).

Assuming a Cs···O distance of 320 pm[8] and for the DME ligand a dihedral angle ω(OC–CO) ≈ 80° for a potential DME chelation results in a presumably unrealistic chelate angle ∠O···Cs···O ≈ 52° (Figure 2a). Furthermore, possibly more than one DME ligand[14] would be required for sufficient Cs$^+$(DME)$_n$ solvation because of the usually rather high Cs coordination numbers of >8.[8]

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(12) AM 1: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. MNDO: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(13) Bock, H.; Ruppert, K.; Havlas, Z.; Fenske, D. *Angew. Chem.* **1990**, *102*, 1095; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1042 (ref 5).

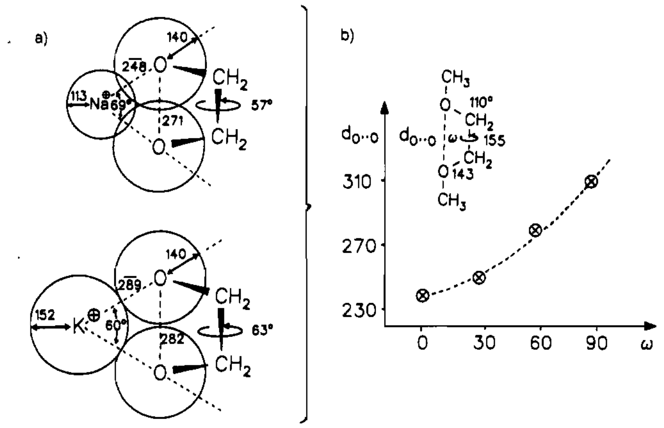

Figure 2. (a) Structure details for the (Na^+DME) and (K^+DME) chelates in the respective $TCNE^{\bullet -}$ salts (radii for 80% ionic character of $Met^{\delta +}$ (Figure 1) and the oxygen center interference radii). (b) Approximate correlation between the bite distance $d_{O\cdots O}$ and the dihedral angle ω-(OC–CO) of DME.

An extensive literature search for Cs organic compounds provides inter alia the following information: Pentamethyldiethylenetriamine (PMDTA) does indeed effectively solvate Cs^+ with three Cs⋯N contacts and, if spatial arrangement allows, one additional Cs⋯C contact.[15] Crown ethers, of which 18-K-6 is too small for a Cs^+ to be placed inside the cavity, can form up to 10-fold coordinated Cs^+ sandwiches with Cs⋯O contact distances between 330 and 345 pm.[16] The more essential rationale for the missing $Cs^+(DME)_n$ solvation, however, seems to be convincingly established by known structures of solvent-free Cs^+ salts of polycyano-substituted planar radical anions such as pentacyanopropenide,[17] $[(NC)_5C_3^-Cs^+]_\infty$, or tetracyano-*p*-quinodimethanide,[18]$[\{(NC)_2CC_6H_4C(CN)_2^{\bullet -}\}_2Cs_2^+(NC)_2CC_6H_4C(CN)_2]_\infty$: It might be the preferential packing achieved by stacking of the π-disks in vertical sheets which enforces a crystal growth from solution with loss of the only weakly bound Cs^+ solvent shell (Figure 1a).

Crystal Packing in $[TCNE^{\bullet -}Cs^+]^{\bullet}_\infty$. The monoclinic structure (space group $P2_1/n$) determined shows each eight radical anions and Cs^+ countercations in the unit cell (Figure 3).

The $TCNE^{\bullet -}$ anions are packed in stacks, which are considerably shifted relative to each other and partly intercalated (Figure 3). Comparison with the (Na^+DME) and (K^+DME) salts reveals essential differences (Figure 4): If the tilt of the $TCNE^{\bullet -}$ ions is chosen for reference, their central CC bonds are stacked in the same direction in both the (K^+DME) and Cs^+ salts but are stacked perpendicular in the (Na^+DME) salt (Figure 4b). In both the sodium and potassium salts, the solvated countercations are intercalated within each pair of $TCNE^{\bullet -}$ layers exhibiting the shorter distance (Figure 4a), whereas in the Cs^+ salt, which shows the largest distortion with respect to the stacking axis (Figure 4b), no such ordered intercalation is observed (Figures 3b and 4a): The Cs^+ ions connect both the stacks and the adjacent $TCNE^{\bullet -}$ ions within them.

Crystal Packing in Other Cs^+ Salts of Polycyano-Substituted Organic Anions. The known structures of both cesium pentacyanopropenide[17] (Figure 5a) and cesium tetracyano-*p*-quinodimethanide (TCNQ)[18] (Figure 5b) are well-suited for a comparison with the packing in $[TCNE^{\bullet -}Cs^+]$ (Figures 3 and 4).

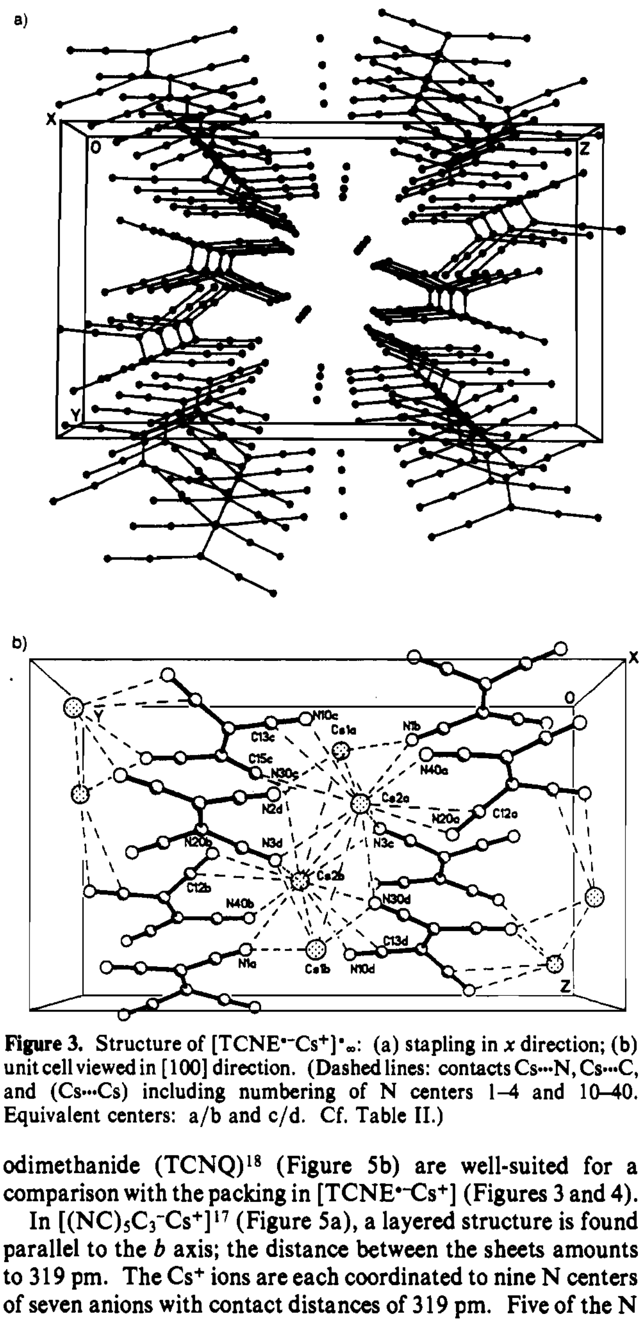

Figure 3. Structure of $[TCNE^{\bullet -}Cs^+]^{\bullet}_\infty$: (a) stapling in *x* direction; (b) unit cell viewed in [100] direction. (Dashed lines: contacts Cs⋯N, Cs⋯C, and (Cs⋯Cs) including numbering of N centers 1–4 and 10–40. Equivalent centers: a/b and c/d. Cf. Table II.)

In $[(NC)_5C_3^-Cs^+]$[17] (Figure 5a), a layered structure is found parallel to the *b* axis; the distance between the sheets amounts to 319 pm. The Cs^+ ions are each coordinated to nine N centers of seven anions with contact distances of 319 pm. Five of the N centers are in a plane and two each are above and below. The anions are each surrounded by eight Cs^+ ions, of which four are in a plane and two each are above and below. The sodium and potassium salts, $[(NC)_5C_3^-Met^+]$, are also known.[8] In contrast to the respective $TCNE^{\bullet -}$ salts and $[(NC)_2CC(CN)_2^{\bullet -}(Met^+DME)]$ salts they also crystallize solvent-free.

The seemingly nonstoichometric $(TCNQ)_3Cs_2$ compound contains two different TCNQ moieties: two radical anions and one neutral molecule. It also crystallizes in stacks (Figure 5b) with comparable layer distances of 321 and 326 pm, i.e. without a specific dimer substructure (cf. Figure 4). The Cs^+ ions are coordinated cubically to eight N centers of four TCNQ moieties belonging to four different stacks; the Cs⋯N contact distances range from 307 to 349 pm. As for the pentacyanopropenide, solvent-free sodium and potassium salts, $[TCNQ^{\bullet -}Met^+]$,[8] are also known, in which the Na^+ is 6-fold and the K^+ 8-fold coordinated.

Cs^+ Coordination. Separation of the two different Cs^+ centers within the unit cell (Figure 2b) according to contact distances

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(14) Cf. e.g. $Na^+(DME)_2$ in the dimeric fluorenone radical anion salt (Bock, H.; Herrmann, H.-F.; Fenske, D.; Goesmann, H. *Angew. Chem.* **1988**, *100*, 1125; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1067) or $Na^+(DME)_3$ in the solvent-separated tetraphenylbutadiene dianion salt (Bock, H.; Näther, C.; Ruppert, K.; Havlas, Z. *J. Am. Chem. Soc.* **1992**, *114*, 6907).

(15) Gregory, K.; Bremer, M.; Schleyer, P. v. R.; Klusener, P. A. A.; Brandsma, L. *Angew. Chem.* **1989**, *101*, 1261; *Angew. Chem., Int. Ed. Engl.* **1989**, *27*, 1224.

(16) Cf. e.g.: Dawes, S. B.; Ward, D. L.; Huang, R. E.; Dye, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 3534.

(17) Hipps, K. W.; Geiser, U.; Mazur, U.; Willet, R. D. *J. Phys. Chem.* **1984**, *88*, 2498.

(18) Fritchie, C. J., Jr.; Arthur, P., Jr. *Acta Crystallogr.* **1966**, *21*, 139 and references therein.

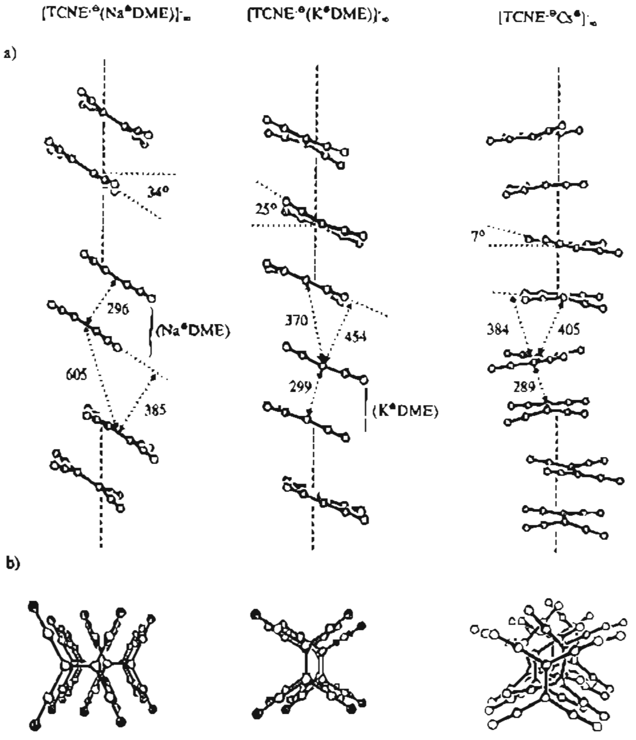


Figure 4. Comparison of the stacking in (Na$^+$DME),[6] (K$^+$DME), and Cs$^+$ salts of TCNE$^{\bullet-}$ (a) perpendicular to and (b) in the stack axes: axes, dashed lines; tilts, dotted lines. (Cf. text.)

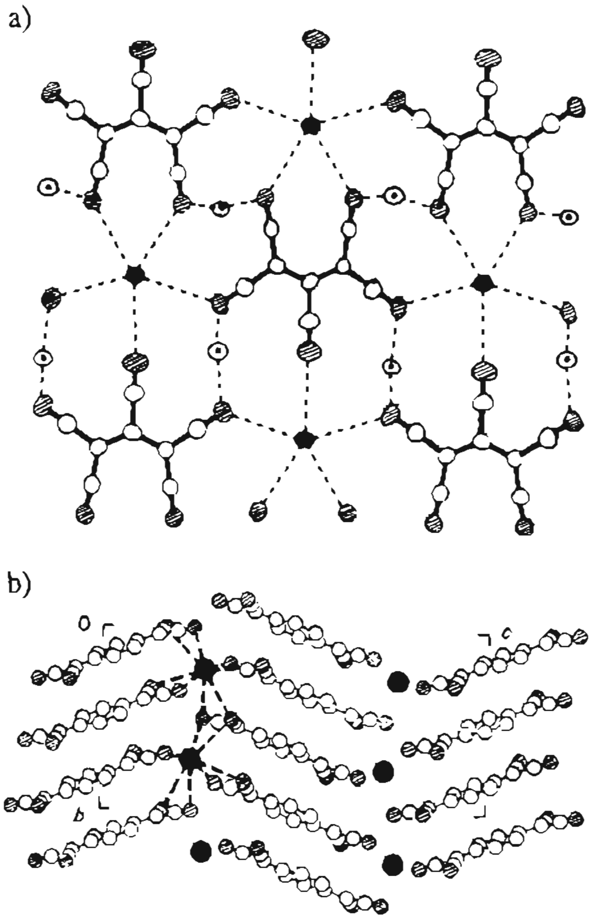
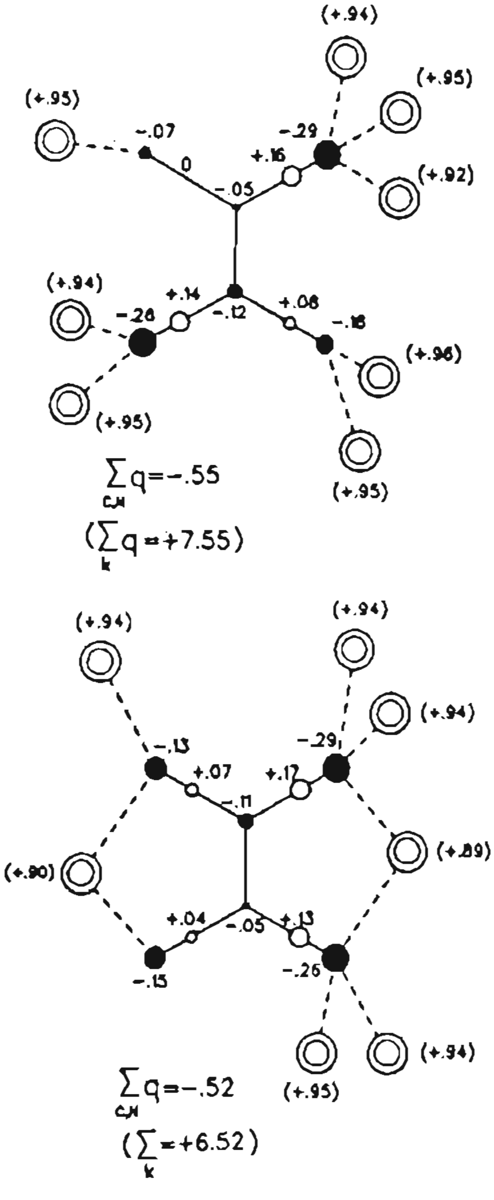


Figure 5. Crystal packing in (a) $[(NC)_3C_3^-Cs^+]_\infty$ (sheet segment parallel to [010] and [101][17]) and (b) $[(TCNQ^{\bullet-})_2Cs_2^+(TCNQ)]_\infty$ ([100] projection[18]): shaded circles, N; solid circles, Cs.

Cs···N < 348 pm and Cs$^{\delta+}$···Cs$^{\delta+}$ < 490 pm yields their coordination spheres (Figure 6). Accordingly, Cs(1) is 8-fold N-coordinated to eight different TCNE$^{\bullet-}$ ions with contact distances Cs···N between 316 and 339 pm and Cs(2) is 9-fold N-coordinated to seven TCNE$^{\bullet-}$ ions (Figure 6: twice vicinal to N(30b)/N(10b) and N(20a)/N(40a)) with contact distances ranging from 313 to 348 pm. Which of the four Cs···Cs neighborhoods, 460–490 pm (Cs(1)) and 454–490 pm (Cs(2)), are considered as additional contacts, depends on definition: the covalent distance Cs–Cs amounts to 456 pm[7] and the sum of two atomic radii is 530 pm, whereas for 80% ionic character 376 pm is calculated[8] and the sum of two ionic radii is as short as 338 pm (Figure 1b).

TCNE Radical Anion Structures. $[TCNE^{\bullet-}Cs^+]_\infty$ contains two different radical anions, which are surrounded by either eight or seven Cs$^+$ countercations and which exhibit significant structural differences (Figure 7 and Table II).

Most surprising is the variation of the central CC bond length: it amounts to 141 pm in the 8-fold Cs$^+$-complexed species (Figure 7A; average contact distance Cs···N = 329 pm) vs 145 pm in the 7-fold Cs$^+$-embedded one (Figure 7B; Cs···N = 327 pm) and indicates a different charge transfer with the less Cs$^+$-coordinated species being the more negative one. This assumption is substantiated by MNDO open-shell calculations, which have been performed on the basis of the experimental structures using the sodium or the potassium parameters[13] and which yield the following approximate charge distributions and total charges:



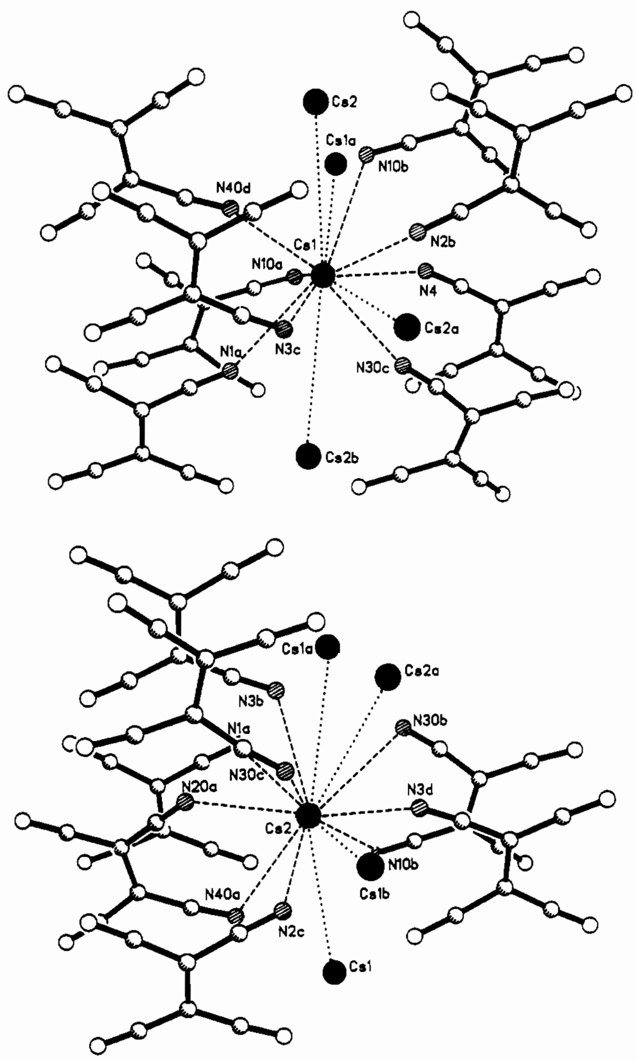


Figure 6. Coordination spheres of Cs(1) and Cs(2). (Cf. Table II and Figure 2b.)

The negative charge at the individual nitrile N centers increases with the number of polarizing countercations, and the same holds for the positive charges at the nitrile C centers. Only small negative charges are predicted for the central CC bond. The total negative charge of the TCNE$^{\bullet-}$ radical anions is almost independent of the number of metal cations coordinated, the positive charge of which is slightly reduced. Summarizing, the charge distribution approximated also supports the assumption that the ions within the $[Cs^+TCNE^{\bullet-}]_\infty$ lattice interact considerably.

Further and presumably interconnected structure variations between TCNE$^{\bullet-}$ ions A and B (Figure 7) concern the longer C–CN bond distances in A (143 vs 141 pm). In addition, some pecularities are found in both A and B as, for instance, the bonding angles ∠CCN of 174° (A) and 173° to the 3-fold Cs$^+$-coordinated cyano substitutent or the unexpectedly large dihedral angle between the molecular $(NC)_2C$ halves of 19°. In general, the twisting of the $(NC)_2C$ molecular halves relative to each other and the elongation of the CC bond between them are the most characteristic structural changes accompanying the reduction of TCNE[19] via its radical anion TCNE$^{\bullet-}$ [1,3,6] to its cyanine-like distorted[5] dianion TCNE^{2-} (Table IV).

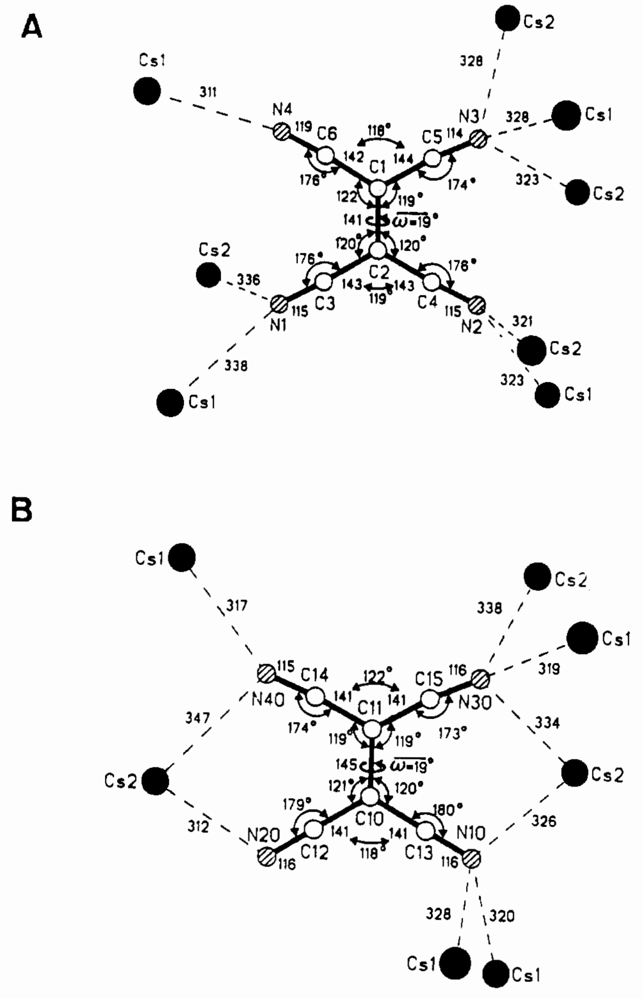


Figure 7. Structures of the two different TCNE$^{\bullet-}$ moieties surrounded by eight (A) or seven (B) Cs$^+$ ions.

The structural changes upon TCNE reduction (Table IV) are arranged according to the increase of the rather sensitive dihedral angle ω(NC–CC–CN) between the two $(NC)_2C$ subunits, which varies from 0° in the neutral molecule[19] to almost 90° in the dianion.[1] The latter is cyanine-like distorted into two negatively charged subunits $(NC)_2C^-$, twisted perpendicular to each other and connected by a CC single bond stretched by 13 pm to 149 pm (Table IV). Single central CC bonds are also found in other ethylene dianions such as the tetraphenyl-substituted one.[20] Simultaneously, the C–CN bonds are shortened. These structural changes upon electron insertion into TCNE as reproduced by geometry-optimized MNDO calculations[6] are shown in Scheme I. The resulting charge distributions suggest that in both TCNE$^{\bullet-}$ and TCNE^{2-} the additional negative charges are predominantly localized at the N centers of highest effective nuclear charge, which are, therefore, the preferred docking sites for countercations.

Summary and Conclusions

The structure determined for the cesium salt of the tetracyanoethylene radical anion exhibits the following interesting facets: In contrast to the analogous sodium and potassium salts $[TCNE^{\bullet-}(Met^+DME)]^\bullet$, and despite single-crystal growth under comparable conditions from DME solution, $[TCNE^{\bullet-}Cs^+]^\bullet$ does not contain a chelating DME ligand. This is presumably due to the preferred stacking of the planar TCNE$^{\bullet-}$ in layers, which cannot intercalate the rather large Cs$^+$ cations as observed for the Cs$^+$ salts of other polycyano-substituted planar π radical

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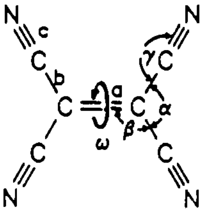
(19) TCNE structure determination may be found in the following references. Cubic modification: (a) Bekoe, D. A.; Trueblood, K. N. *Z. Kristallogr.* **1959**, *113*, 1. (b) Little, R. G.; Pautler, D.; Copens, P. *Acta Crystallogr., Sect. B* **1971**, *27*, 1493. (c) Becker, P.; Coppens, P.; Ross, F. K. *J. Am. Chem. Soc.* **1973**, *95*, 7604. Monoclinic modification: (d) Drück, U.; Guth, H. *Z. Kristallogr.* **1982**, *161*, 103. Gas-phase electron diffraction: (e) Hope, H. *Acta Chem. Scand.* **1968**, *22*, 1057.

(20) Bock, H.; Ruppert, K.; Fenske, D. *Angew. Chem.* **1989**, *101*, 1717; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1685.

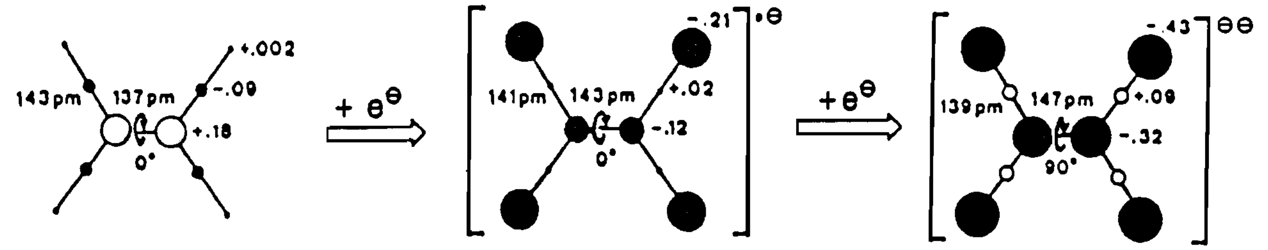
Table IV. Selected Structural Parameters for TCNE[19] and Its $TCNE^{\bullet-}$ [1,3,6] as Well as $TCNE^{2-}$ [1] Salts with the Cations Specified[a]



	TCNE	$TCNE^{\bullet-}$					$TCNE^{2-}$
		$(Cp^*_2Fe)^{\bullet+}$	(Na^+DME)	(K^+DME)	$Cs^+(A)$	$Cs^+(B)$	$(Cp^*_2Co^+)_2$
d_{CC} (*a*)	136	139	142	142	141	145	149
d_{C-CN} (*b*)	143	142	142	142	143	141	139
d_{CN} (*c*)	117	114	115	114	115	116	117
NC–C–CN (α)	116	118	118	118	119	118/22	117
NC–C–C (β)	122	*b*	121	121	119/22	119/21	*b*
CCN (γ)	178	180	178	178/9	174/6	173/9	178
NC–CC–CN (ω)	0	0	8	12	19	19	87

[a] Values are given in whole picometers and degrees. [b] Not reported; cf. text.

Scheme I



anions. Thus the DME solvent is lost on crystallization of the contact ion pairs formed in solution within a monomer ↔ dimer equilibrium.[21]

$[TCNE^{\bullet-}Cs^+]^{\bullet}_{\infty}$ contains two different types of Cs^+ ions, coordinated to eight N centers of eight $TCNE^{\bullet-}$ ions or to nine of seven. In addition, two different $TCNE^{\bullet-}$ ions are found, surrounded by either eight or seven Cs^+ ions. They exhibit, for instance, central $C^{\bullet-}C$ bonds of 141- and 145-pm lengths, which together with the results of open-shell MNDO calculations suggest different total charges. In addition, the $(NC)_2C$ halves in $TCNE^{\bullet-}$ are twisted relative to each other by 19°. Thus, the structural data further confirm $TCNE^{\bullet-}$ as a single-electron-transfer intermediate between the planar TCNE and the twisted $TCNE^{2-}$, a dianion with a central CC single bond of 149-pm length between the perpendicular molecular halves, in which each one negative charge is cyanine-like and energetically favorably delocalized.

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Registry No. Cs, 7440-46-2; TCNE, 670-54-2; cesium tetracyanoethylenide, 12192-60-8.

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(21) Cf. e.g.: Itoh, M. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1947.