of the fully charge separated D$^+$–P–A$^-$ species cannot be time-resolved.

Better results (i.e., a higher efficiency of formation and a longer lifetime for D$^+$–P–A$^-$) could perhaps be obtained by modifying the DPAA–Ru(ttp)$_2^{2+}$–MV^{2+} system as follows: (i) to use a slightly better donor than –DPAA, in order to increase the rate of reaction 4′D; (ii) to use an acceptor more difficult to reduce than –MV^{2+}, so as to increase the energy gap between D$^+$–P–A$^-$ and the ground state, which would decrease the rate of the CR reaction 7 (Marcus inverted behavior); (iii) to increase the separation between P and MV^{2+}, so as to decrease the electronic factor for reaction 7.

Acknowledgment. We thank P. Staub, L. Minghetti, and G. Gubellini for technical assistance. This work was supported by the Centre Nationale de la Recherche Scientifique and Ministere de la Recherche (France) and by the Programma Finalizzato Chimica Fine II, Consiglio Nazionale delle Ricerche, and Ministero dell' Universitá e della Ricerca Scientifica e Tecnologica (Italy).

Registry No. ttp, 89972-77-0; ttp hydrobromide salt, 136247-29-5; Fe(ttp)$_2$(PF$_6$)$_2$, 136247-59-1; 6′-t-2,2′:4′,2″-tp, 136247-30-8; ttp-Br, 89972-78-1; ttp-MV^{2+}·2NO$_3^-$, 136247-31-9; ttp-MV^{2+}·2Cl$^-$, 136247-32-0; ttp-MV^{2+}·2PF$_6^-$, 136247-34-2; ttp-PTZ, 124598-56-7; ttp-DPAA, 136247-34-2; Ru(ttp)Cl$_3$, 136276-24-9; [Ru(ttp)$_2$](PF$_6$)$_2$, 121810-60-4; [Ru(ttp)$_2$]$^{3+}$, 121810-63-7; [Ru(ttp)$_2$]$^+$, 121810-62-6; [PTZ-Ru(ttp)$_2$](PF$_6$)$_2$, 136247-49-9; [PTZ-Ru(ttp)$_2$]$^{4+}$, 136247-42-2; [PTZ-Ru(ttp)$_2$]$^{3+}$, 136247-46-6; [PTZ-Ru(ttp)$_2$]$^+$, 136247-36-4; [DPAA-Ru(ttp)$_2$](PF$_6$)$_2$, 136247-51-3; [DPAA-Ru(ttp)$_2$]$^{4+}$, 136247-43-3; DPAA-Ru(ttp)$_2^{3+}$, 136247-45-5; DPAA-Ru(ttp)$_2^+$, 136276-21-6; [Ru(ttp)$_2$-MV](PF$_6$)$_4$, 136247-52-4; [Ru(ttp)$_2$-MV]$^{5+}$, 136247-58-0; [Ru(ttp)$_2$-MV]$^{3+}$, 136247-39-7; [Ru(ttp)$_2$-MV]$^+$, 136247-35-3; Ru(ttp-MV^{2+})$_2$(PF$_6$)$_6$, 136247-54-6; [PTZ-Ru(ttp)$_2$-MV](PF$_6$)$_4$, 136247-55-7; [PTZ-Ru(ttp)$_2$-MV]$^{6+}$, 136276-22-7; [PTZ-Ru(ttp)$_2$-MV]$^{5+}$, 136247-47-7; [PTZ-Ru(ttp)$_2$-MV]$^{3+}$, 136247-40-0; [PTZ-Ru(ttp)$_2$-MV]$^+$, 136247-37-5; [DPAA-Ru(ttp)$_2$-MV](PF$_6$)$_4$, 136247-57-9; [DPAA-Ru(ttp)$_2$-MV]$^{6+}$, 136247-44-4; [DPAA-Ru(ttp)$_2$-MV]$^{5+}$, 136276-23-8; [DPAA-Ru(ttp)$_2$-MV]$^{3+}$, 136247-41-1; [DPAA-Ru(ttp)$_2$-MV]$^+$, 136247-38-6; acetamide, 60-35-5; *p*-tolylaldehyde, 104-87-0; 2-acetylpyridine, 1122-62-9; Mohr's salt, 10045-89-3; 1-methyl-4,4′-bipyridinium iodide, 38873-01-7; phenothiazine, 92-84-2; 4-(*N*,*N*-di-*p*-anisoylamino)benzaldehyde, 89115-20-8.

Contribution from the Departments of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada,
and University of Toronto, Toronto, Ontario M5S 1A1, Canada

Crystal Structures of Potassium Cryptated Salts of the TeSe$_2^{2-}$, Pyramidal TeSe$_3^{2-}$, and Mixed Compounds Containing Pyramidal TeSe$_3^{2-}$ and Chain Te$_x$Se$_{4-x}^{2-}$ Anions and ^{77}Se and ^{125}Te Solution NMR Studies of the Pyramidal Selenothiotellurite Anions TeS$_m$Se$_{3-m}^{2-}$ (m = 0–3)

Már Björgvinsson,[1a] Jeffery F. Sawyer,*[,1b] and Gary J. Schrobilgen*[,1a]

Received August 9, 1990

The preparation of several compounds containing mixed tellurium–selenium and tellurium–sulfur–selenium anions as cryptated potassium salts [crypt ≡ 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane] are reported along with the X-ray crystal structures of four compounds (**1**–**4**) containing Te–Se dianions. Compound **1** (2,2,2-crypt-K$^+$)$_2$TeSe$_2^{2-}$·en, crystallizes in the triclinic space group *P*1 with a = 10.9725 (8) Å, b = 12.1940 (9) Å, c = 12.3242 (10) Å, α = 59.182 (7)°, β = 73.781 (7)°, γ = 67.718 (6)°, V = 1303 Å^3, D_x = 1.500 g cm^{-3} for Z = 1, and R (R_w) = 0.0382 (0.0465) for 4459 observed [$I \geq 3\sigma(I)$] data. Similarly, compound **2**, (2,2,2-crypt-K$^+$)$_2$TeSe$_3^{2-}$·en, crystallizes in the trigonal space group $P3_2$ (No. 145) with a = 12.386 (5) Å, c = 30.669 (15) Å, V = 4076 Å^3, D_x = 1.537 g cm^{-3} for Z = 3, and R (R_w) = 0.0574 (0.0638) for 1810 observed [$I \geq 2.5\sigma(I)$] data. However, compounds **3** and **4** were found to be mixed crystals containing principally the pyramidal TeSe$_3^{2-}$ anion as well as different minor amounts of a chain tetrachalcogen anion, although the overall Te/Se composition of the averaged anion in each compound is essentially constant for the two compounds at Te$_{0.9}$Se$_{3.4}^{2-}$. Compound **3** [values for **4** in brackets] crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with a = 12.252 (4) Å [12.286 (2) Å], b = 21.643 (3) Å [21.587 (9) Å], c = 20.718 (3) Å [20.759 (2) Å], β = 97.45 (2)° [97.61 (1)°], V = 5447 Å^3 [5457 Å^3], and R (R_w) = 0.0733 (0.0730) [0.0667 (0.0632)] for 2150 [2898] observed reflections. In **1**, the Te–Se bond lengths and Se–Te–Se bond angle in the TeSe$_2^{2-}$ anion are 2.501 (1) and 2.504 (1) Å and 111.3 (1)°, respectively, while in **2** the Te–Se bond lengths in the pyramidal TeSe$_3^{2-}$ anion are 2.454 (4), 2.460 (4), and 2.465 (4) Å and the Se–Te–Se bond angles are 104.8 (2), 107.4 (1), and 108.9 (1)°. In compound **3**, the anion site consists of ca. 89% of a pyramidal anion (assumed to be TeSe$_3^{2-}$) and 11% of an open-chain tetrachalcogen anion with all compositions *except TeSe*$_3^{2-}$ being predicted on the basis of NMR data (see preceding paper), while in **4** the pyramidal:chain dianion ratio is ca. 81:19. In addition, the pyramidal-shaped selenothiotellurite anions TeS$_m$Se$_{3-m}^{2-}$ (m = 0–3) have been prepared and characterized in ethylenediamine (en) solutions. Trends in the ^{77}Se and ^{125}Te chemical shifts and in the one-bond spin–spin coupling constants, $^1J(^{125}\text{Te} - {}^{77}\text{Se})$, for the latter species are reported and discussed in terms of the relative electronegativities of sulfur and selenium.

Introduction

In recent years, a large number of homopolychalcogenide anions of selenium and tellurium have been structurally characterized in the solid state.[2-10] However, the heteropolychalcogenide anions of Se and Te have been much less studied. Greiver et al.[11] have reported on the preparation and isolation of the salts of TeSe$_2^{2-}$ and TeSe$_3^{2-}$. However, only the mixed Se/Te polychalcogenide Rb$_2$TeSe$_4$ had been structurally characterized in the solid state at the start of this study.[12] More recently, however, structures of Na$_2$TeSe$_3$ and K$_2$TeSe$_3$ have been reported[13a] along with preliminary details for the compounds [Sr(en)$_4$]TeSe$_3$ and [Ba(en)$_{3.5}$]TeSe$_3$ (en = ethylenediamine),[13b] all of which contain the pyramidal TeSe$_3^{2-}$ anion. The latter abstract also includes some information on the salts (2,2,2-crypt-K)$_2$TeSe$_{10}$ and [(2,2,2-crypt-Ba)(en)]TeSe$_{10}$·0.5en (2,2,2-crypt = 4,7,13,16,21,24-hex-

---

(1) (a) McMaster University. (b) University of Toronto.
(2) Zagler, R.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch.* **1987**, *42B*, 151.
(3) Teller, R. G.; Krause, L. J.; Haushalter, R. C. *Inorg. Chem.* **1983**, *22*, 1809.
(4) Böttcher, P. *Z. Anorg. Allg. Chem.* **1977**, *432*, 167.
(5) Devereux, L. A.; Sawyer, J. F.; Schrobilgen, G. J. *Acta Crystallogr.* **1985**, *C41*, 1730.
(6) König, T.; Eisenmann, B.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1983**, *498*, 99.
(7) Brese, N. E.; Randall, C. R.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 940.
(8) König, T.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch.* **1982**, *37B*, 1245.
(9) Cisar, A.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 632.
(10) Huffman, J. C.; Haushalter, R. C. *Z. Anorg. Allg. Chem.* **1984**, *518*, 203.
(11) Greiver, T. N.; Sal'dau, É. P.; Zaitseva, I. G. *J. Appl. Chem. USSR (Engl. Transl.)* **1971**, *44*, 1502.
(12) Böttcher, P.; Kretschmann, U. *Z. Naturforsch.* **1985**, *40b*, 895.
(13) (a) Zagler, R.; Eisenmann, B. *Z. Kristallogr.* **1988**, *183*, (b) *Ibid.* **1988**, *185*, 473.

0020-1669/91/1330-4238$02.50/0

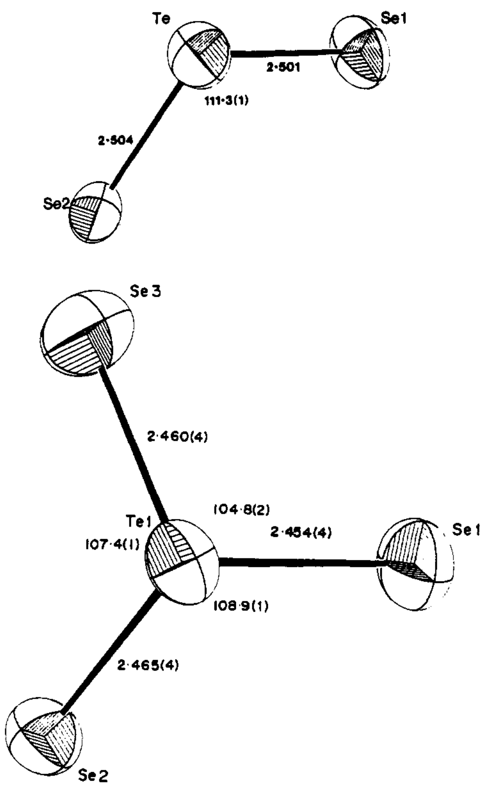


Figure 1. ORTEP views of the $TeSe_2^{2-}$ and pyramidal $TeSe_3^{2-}$ anions including bond distances (Å) and bond angles (deg).

aoxa-1,10-diazabicyclo[8.8.8]hexacosane), which contain the mixed anion $TeSe_{10}^{2-}$, whose structure is based upon two bidentate Se_5^- anions bonded to a central square-planar Te atom and is isostructural with the Se_{11}^{2-} anion.[13c] In a previous paper, we reported on the preparation and structural characterization in solution by ^{77}Se and ^{125}Te NMR spectroscopy of the tri- and tetraheteropolychalcogenide anions Ch_3^{2-} and Ch_4^{2-} (ch = Se and/or Te).[14] The NMR study showed that, except for the $TeSe_3^{2-}$ anion, the tetrachalcogenide anions have open-chain structures. The $TeSe_3^{2-}$ anion was, however, found to have a pyramidal structure with Te bonded to three equivalent Se atoms and is, therefore, isostructural with the thiotellurite anion TeS_3^{2-}.[15–17] Moreover, only one structural isomer was indicated for each of the tri- and tetrachalcogen anions with, in each case, the Se atoms in terminal positions bonded to bridging Te atoms in the open-chain structures or to the central Te atom in the $TeSe_3^{2-}$ anion. It was therefore of interest to determine the detailed structures of some of the mixed Se/Te polychalcogenide anions in their potassium cryptated salts by X-ray crystallography. Furthermore, comparison of the present structure to the recently reported structures of the Na^+ and K^+ salts of the $TeSe_3^{2-}$ anion enables the influence of the crystal environment on the dimensions of this anion to be quantified. Because the TeS_3^{2-} and $TeSe_3^{2-}$ anions had been found to be isostructural, it was considered likely that the mixed $TeS_mSe_{3-n}^{2-}$ anion also would be isostructural; consequently, their preparation and characterization in solution by ^{77}Se and ^{125}Te NMR spectroscopy were undertaken.

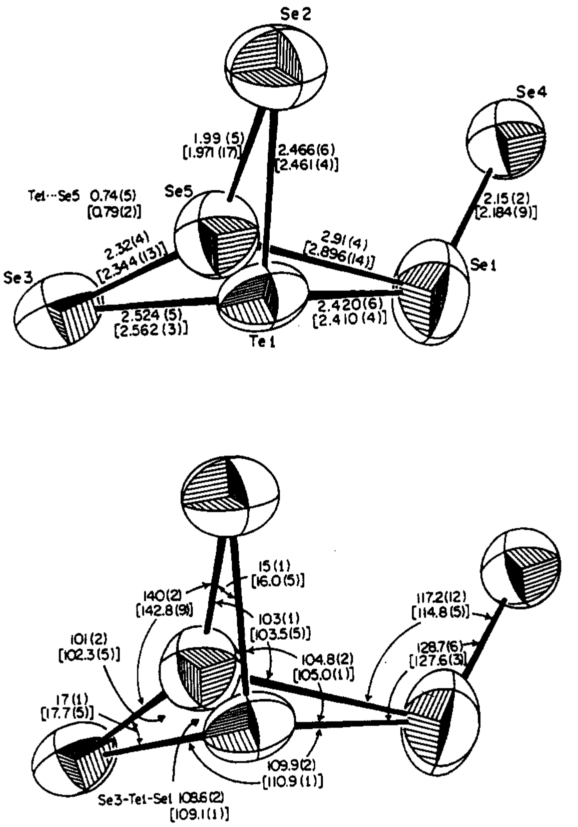
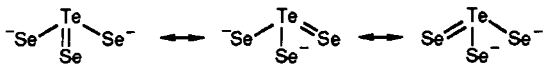


Figure 2. ORTEP view of the disordered arrangement of the anion sites in compounds **3** and **4** including bond distances (Å) and bond angles (deg) with the values for **4** in square brackets. Te and Se atom designations indicate the scattering curves used in the refinements. See Table III and the text for discussions on the compositions of the anions.

Scheme I



Results and Discussion

Crystal Structures. Compounds **1**–**4** were characterized by X-ray crystallography as containing cryptated potassium ions, ethylenediamine solvent, and telluroselenide anions. In **1** and **2** the respective $TeSe_2^{2-}$ and $TeSe_3^{2-}$ anions (Figure 1, Table I) were found to be ordered, and no evidence was found for any other anionic species in the lattices within the precisions of the data sets collected. However, compounds **3** and **4** were observed to be mixed crystals, and the anion sites in the lattices were found to consist of two anion types. The major atom positions are consistent with a pyramidal tetrachalcogen anion, most probably $TeSe_3^{2-}$, while two additional minor atom positions are consistent with the presence of an open chain tetrachalcogen anion. Some atom sites are common to both anion types, and other interpretations of the data, including disorder of the pyramidal $TeSe_3^{2-}$ anion (using Se(5) as the alternative Te position), are possible (see Figure 2, Table III, and discussion below). This is also consistent with the accompanying ^{77}Se and ^{125}Te NMR studies,[14] which have shown the presence of large amounts of the $TeSe_3^{2-}$ anion in the mixture of $Te_nSe_{4-n}^{2-}$ (n = 1–4) anions present in the solutions from which **3** and **4** were isolated. However, similar solution studies indicated that the $TeSe_2^{2-}$ and $TeSe_3^{2-}$ anions were the major polychalcogenide anions present in the solutions from which **1** and **2** were isolated.

In **1** and **2**, the most interesting aspects of the structures are the new telluroselenide anions: the V-shaped $TeSe_2^{2-}$ anion and the trigonal pyramidal $TeSe_3^{2-}$ anion (Figure 1). In **2** the Te atom is 0.914 (2) Å above the Se_3 plane of the $TeSe_3^{2-}$ anion. In both anions the Te–Se bond lengths are shorter than the single Te–Se bond length of 2.53 Å given by Pauling.[18] This is especially true for the $TeSe_3^{2-}$ anion since the Te–Se distance of 2.46 Å is 0.07 Å shorter than the above value but is consistent with a bond order of $^4/_3$ resulting from equal contributions of the resonance structures

---

[14] Björgvinsson, M.; Schrobilgen, G. J. *Inorg. Chem.* **1991**, *30*, 2540.

[15] Gerl, H.; Eisenmann, B.; Roth, P.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1974**, *407*, 135.

[16] Jumas, J.-C.; Ribes, M.; Maurin, M.; Philippot, E. *Acta Crystallogr.* **1976**, *B32*, 444.

[17] Dittmar, G.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1978**, *439*, 212.

[18] Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 93.

[19] Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.

Table I. Final Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations in Parentheses for $[2,2,2\text{-crypt-K}]_2\text{TeSe}_2\cdot\text{en}$ (**1**)

atom	*x*	*y*	*z*	B_{eq}, Å^2
Te1	1.00000	1.00000	1.0000	5.65 (2)
Se1	0.86303 (9)	1.18751 (9)	0.82590 (8)	6.48 (3)
Se2	1.24239 (8)	0.96906 (7)	0.92779 (7)	4.73 (2)
K1	0.2265 (1)	0.6348 (1)	0.6011 (1)	3.36 (4)
N11	−0.0624 (5)	0.7255 (5)	0.6053 (5)	4.5 (2)
C12	−0.1116 (8)	0.8689 (7)	0.5667 (8)	6.4 (3)
C13	−0.053 (1)	0.9117 (7)	0.6310 (8)	7.3 (3)
O14	0.0833 (5)	0.8905 (4)	0.5952 (4)	5.0 (1)
C15	0.1395 (9)	0.9220 (6)	0.6614 (7)	6.6 (3)
C16	0.2817 (9)	0.9060 (7)	0.6197 (7)	6.9 (2)
O17	0.3483 (5)	0.7671 (4)	0.6465 (4)	5.0 (1)
C18	0.4866 (8)	0.7448 (7)	0.6174 (7)	7.2 (2)
C19	0.5531 (7)	0.6025 (8)	0.6567 (7)	6.6 (3)
N110	0.5172 (5)	0.5465 (5)	0.5912 (5)	4.7 (2)
C111	0.5761 (8)	0.5992 (9)	0.4578 (7)	6.9 (3)
C112	0.5228 (8)	0.5743 (7)	0.3763 (6)	6.1 (2)
O113	0.3854 (5)	0.6415 (4)	0.3736 (4)	5.0 (1)
C114	0.3300 (8)	0.6220 (7)	0.2954 (6)	5.7 (2)
C115	0.1923 (7)	0.7024 (6)	0.2823 (6)	5.0 (2)
O116	0.1136 (5)	0.6641 (4)	0.4020 (4)	4.7 (1)
C117	−0.0199 (8)	0.7398 (7)	0.3903 (7)	5.9 (2)
C118	−0.0983 (7)	0.6963 (7)	0.5174 (7)	5.8 (2)
C119	−0.1183 (7)	0.6482 (8)	0.7369 (7)	6.1 (3)
C120	−0.0556 (7)	0.5036 (7)	0.7953 (7)	6.0 (2)
O121	0.0752 (4)	0.4760 (4)	0.8119 (4)	4.7 (1)
C122	0.1405 (8)	0.3380 (6)	0.8575 (6)	5.1 (2)
C123	0.2748 (8)	0.3101 (7)	0.8806 (6)	5.5 (2)
O124	0.3505 (5)	0.3760 (4)	0.7652 (4)	5.1 (2)
C125	0.4832 (8)	0.3411 (8)	0.7806 (8)	6.6 (3)
C126	0.5618 (8)	0.4028 (8)	0.6558 (8)	6.8 (3)
K2	0.3175 (1)	0.2830 (1)	0.2516 (1)	3.62 (4)
N21	0.6096 (6)	0.1939 (5)	0.2422 (5)	4.6 (2)
C22	0.6588 (8)	0.0530 (7)	0.2754 (7)	6.2 (3)
C23	0.5992 (9)	0.0125 (7)	0.2104 (7)	6.4 (3)
O24	0.4603 (5)	0.0292 (4)	0.2553 (4)	5.2 (1)
C25	0.3959 (8)	−0.0011 (6)	0.1925 (6)	5.8 (2)
C26	0.2563 (8)	0.0150 (6)	0.2379 (7)	6.1 (2)
O27	0.1919 (5)	0.1507 (4)	0.2078 (4)	4.9 (1)
C28	0.0524 (8)	0.1769 (7)	0.2310 (7)	6.5 (2)
C29	−0.0094 (7)	0.3218 (7)	0.1907 (7)	5.9 (2)
N210	0.0271 (6)	0.3706 (5)	0.2603 (5)	4.8 (2)
C211	−0.0291 (8)	0.3138 (8)	0.3941 (8)	6.6 (3)
C212	0.0271 (8)	0.3364 (8)	0.4759 (7)	6.4 (3)
O213	0.1643 (5)	0.2749 (4)	0.4770 (4)	5.1 (1)
C214	0.2200 (8)	0.2851 (7)	0.5629 (6)	6.0 (2)
C215	0.3581 (8)	0.2039 (7)	0.5741 (6)	5.5 (2)
O216	0.4346 (5)	0.2502 (4)	0.4507 (4)	4.6 (1)
C217	0.5660 (8)	0.1733 (7)	0.4608 (7)	5.8 (2)
C218	0.6472 (7)	0.2173 (7)	0.3314 (7)	5.3 (2)
C219	0.6643 (7)	0.2729 (8)	0.1116 (7)	5.8 (3)
C220	0.5975 (7)	0.4175 (7)	0.0501 (7)	5.7 (2)
O221	0.4651 (4)	0.4446 (4)	0.0399 (4)	4.5 (1)
C222	0.3955 (8)	0.5836 (6)	−0.0081 (6)	5.1 (2)
C223	0.2625 (8)	0.6109 (6)	−0.0299 (6)	5.0 (2)
O224	0.1901 (5)	0.5436 (4)	0.0882 (4)	4.9 (1)
C225	0.0545 (8)	0.5832 (7)	0.0722 (7)	5.9 (3)
C226	−0.0221 (8)	0.5161 (8)	0.2034 (8)	6.2 (3)
N1S	0.577 (2)	0.848 (1)	0.837 (1)	19.2 (6)[a]
N2S	0.665 (2)	0.959 (2)	0.863 (2)	29 (1)[a]
C1S	0.616 (2)	0.777 (1)	0.977 (2)	15.2 (6)[a]
C2S	0.697 (2)	0.858 (2)	0.984 (2)	21.4 (9)[a]

[a] Atom refined with isotropic *B*'s.

Table II. Final Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations in Parentheses for $[2,2,2\text{-crypt-K}]_2\text{TeSe}_3\cdot\text{en}$ (**2**)

atom	*x*	*y*	*z*	B_{eq}, Å^2
Te1	0.0589 (2)	0.2559 (2)	0.642	4.00 (5)
Se1	0.1959 (3)	0.1993 (3)	0.6024 (1)	6.9 (1)
Se2	0.0616 (3)	0.2104 (3)	0.7201 (1)	5.16 (9)
Se3	−0.1517 (3)	0.1115 (3)	0.6143 (1)	6.9 (1)
K1	0.8329 (5)	0.2692 (5)	0.0571 (2)	3.8 (2)
N11	0.819 (2)	0.281 (2)	−0.0373 (8)	4.9 (6)[a]
C12	0.946 (3)	0.373 (3)	−0.053 (1)	8 (1)[a]
C13	1.006 (3)	0.502 (3)	−0.030 (1)	6.9 (9)[a]
O14	1.026 (2)	0.484 (1)	0.0150 (6)	5.0 (5)[a]
C15	1.074 (3)	0.597 (3)	0.038 (1)	6.4 (9)[a]
C16	1.108 (2)	0.579 (2)	0.081 (1)	4.1 (7)[a]
O17	1.000 (2)	0.483 (2)	0.1040 (7)	5.4 (5)[a]
C18	1.026 (3)	0.470 (3)	0.147 (1)	6.1 (8)[a]
C19	0.918 (3)	0.388 (3)	0.173 (1)	8 (1)[a]
N110	0.850 (2)	0.256 (2)	0.1541 (9)	5.9 (7)[a]
C111	0.721 (3)	0.188 (3)	0.173 (1)	6.3 (9)[a]
C112	0.632 (3)	0.227 (3)	0.152 (1)	6.6 (9)[a]
O113	0.619 (2)	0.210 (1)	0.1078 (6)	4.8 (5)[a]
C114	0.541 (3)	0.255 (3)	0.091 (1)	6.2 (9)[a]
C115	0.515 (2)	0.216 (2)	0.044 (1)	5.4 (8)[a]
O116	0.632 (2)	0.281 (1)	0.0209 (7)	5.2 (5)[a]
C117	0.614 (3)	0.254 (3)	−0.025 (1)	7.1 (9)[a]
C118	0.733 (3)	0.330 (3)	−0.049 (1)	6.1 (9)[a]
C119	0.790 (3)	0.163 (3)	−0.058 (1)	7 (1)[a]
C120	0.856 (3)	0.102 (3)	−0.040 (1)	8 (1)[a]
O121	0.829 (2)	0.072 (2)	0.0048 (7)	5.8 (5)[a]
C122	0.887 (2)	0.008 (2)	0.025 (1)	5.2 (8)[a]
C123	0.857 (2)	−0.015 (2)	0.069 (1)	5.1 (8)[a]
O124	0.883 (1)	0.093 (1)	0.0938 (6)	4.8 (5)
C125	0.869 (3)	0.073 (3)	0.140 (1)	8 (1)[a]
C126	0.917 (3)	0.188 (3)	0.163 (1)	6.3 (9)[a]
K2	0.1178 (5)	0.5136 (5)	0.4197 (2)	3.3 (2)
N21	0.162 (2)	0.534 (2)	0.3222 (8)	5.2 (6)[a]
C22	0.089 (3)	0.401 (3)	0.303 (1)	9 (1)[a]
C23	−0.034 (3)	0.323 (3)	0.324 (1)	7 (1)[a]
O24	−0.034 (1)	0.306 (1)	0.3690 (6)	4.5 (4)[a]
C25	−0.155 (2)	0.223 (2)	0.3847 (9)	4.1 (7)[a]
C26	−0.150 (3)	0.198 (3)	0.432 (1)	6.1 (8)[a]
O27	−0.102 (1)	0.310 (1)	0.4558 (6)	4.2 (4)[a]
C28	−0.100 (2)	0.292 (2)	0.500 (1)	5.2 (8)[a]
C29	−0.054 (3)	0.403 (3)	0.526 (1)	6.1 (9)[a]
N210	0.076 (2)	0.500 (2)	0.5162 (8)	5.1 (6)[a]
C211	0.099 (2)	0.621 (2)	0.532 (1)	4.8 (7)[a]
C212	0.044 (2)	0.684 (2)	0.505 (1)	5.3 (8)[a]
O213	0.101 (1)	0.714 (1)	0.4625 (6)	4.2 (4)[a]
C214	0.042 (2)	0.764 (2)	0.4323 (9)	3.7 (7)[a]
C215	0.104 (3)	0.797 (3)	0.390 (1)	6.0 (8)[a]
O216	0.100 (1)	0.696 (2)	0.3697 (7)	5.2 (5)[a]
C217	0.162 (2)	0.725 (2)	0.331 (1)	4.8 (8)[a]
C218	0.112 (2)	0.604 (2)	0.305 (1)	5.5 (8)[a]
C219	0.293 (3)	0.578 (3)	0.315 (1)	7 (1)[a]
C220	0.362 (3)	0.538 (3)	0.342 (1)	7.0 (9)[a]
O221	0.352 (1)	0.563 (1)	0.3861 (6)	4.6 (5)[a]
C222	0.424 (3)	0.533 (3)	0.414 (1)	8 (1)[a]
C223	0.419 (2)	0.569 (2)	0.457 (1)	5.8 (8)[a]
O224	0.295 (2)	0.501 (2)	0.4756 (7)	5.8 (5)[a]
C225	0.295 (3)	0.533 (3)	0.518 (1)	7 (1)[a]
C226	0.162 (3)	0.463 (3)	0.538 (1)	6.4 (9)[a]
N1S	0.267 (4)	1.001 (3)	0.166 (1)	15 (1)[a]
N2S	0.067 (4)	0.994 (4)	0.207 (2)	19 (2)[a]
C1S	0.157 (4)	0.850 (4)	0.184 (2)	14 (2)[a]
C2S	0.064 (5)	0.893 (6)	0.175 (2)	20 (3)[a]

[a] Atom refined with isotropic *B*'s.

shown in Scheme I and a Te–Se distance of 2.445 Å calculated by using the Pauling equation (1), with $r_1(\text{A–B}) = 2.53$ Å and

$$r_n(\text{A–B}) = r_1(\text{A–B}) - 0.60 \log n \qquad (1)$$

$n = {}^4/_3$.[18] Notably, the dimensions of the present TeSe_3^{2-} anions are significantly different from those of the corresponding anion in the salts Na_2TeSe_3 and K_2TeSe_3, with the Te–Se bond lengths [2.492 Å (K^+) and 2.503 Å (Na^+)] being significantly longer by ca. 0.04 Å and the ⟨Se–Te–Se⟩ bond angles [103.4° (K^+) and 101.8° (Na^+)] correspondingly smaller.[13a] Undoubtedly, this is due to anion–cation [$\text{K}^+\cdots\text{Se}$ contacts are ≥3.282 Å, and $\text{Na}^+\cdots\text{Se}$ contacts are ≥2.988 Å] and anion–anion Te⋯Se interactions. In the K^+ salt only two Te⋯Se interactions <4.2 Å occur, at distances of 3.844 and 4.099 Å, approximately *trans* to two of the Te–Se primary bonds, while in the Na^+ salt three somewhat shorter interactions of distances 3.574, 3.595, and 3.636 Å occur, giving an overall distorted-monocapped-octahedral geometry around Te. In the present salt only long-range Te⋯H and Se⋯N(H) contacts are observed (Table IV).

Table III. Population Analysis[a] of the Six Atom Sites in the Anion Positions in Compounds 3 and 4

	compd 3	compd 4		compd 3	compd 4
a, Å	12.252 (4)	12.286 (2)	α, deg	90.0	90.0
b, Å	21.643 (3)	21.587 (9)	β, deg	97.45 (2)	97.61 (1)
c, Å	20.718 (3)	20.759 (2)	γ, deg	90.0	90.0
N_{ref}	2150	2898	abs cor data: R, R_w	0.073; 0.073	0.067; 0.063

atom site	compd 3				compd 4			
	pp	no. of el's	% Te	% Se	pp	no. of el's	% Te	% Se
Te(1)	0.885 (18)	46.0 (10)	67 (6)	33	0.830 (11)	43.2 (6)	51 (3)	49 (3)
Se(1)	1.046 (11)	36.6	9 (2)	91	1.093 (7)	37.2 (2)	18 (1)	82 (1)
Se(2)	0.885 (9)	30.1		89	0.798 (5)	27.1 (2)		80
Se(3)	1.051 (10)	35.7	10 (2)	90	1.081 (6)	36.8 (2)	16 (1)	84 (1)
Se(4)	0.146 (9)	5.0		15	0.214 (6)	7.3 (2)		21
Se(5)	0.169 (26)	5.7		17	0.251 (16)	8.5 (6)		25
tot.			86	335			85	341
		$Te_{0.86}Se_{3.35}$				$Te_{0.85}Se_{3.41}$		

[a] pp = population parameter. No. of el's = number of electrons at each site obtained by multiplying the final pp's by 52 if the scattering curve for Te was used or 34 if that of Se was used. [A similar result for the main Te(1) site was obtained when the scattering curve of Se was employed.] The % Te (% Se) at sites assumed to be mixtures of Te and Se can then be calculated from the following expression: no. of el's = $52x + 34(1 - x)$, where x = fraction of Te at each site or at sites assumed to be only Se by multiplying the population parameter by 100. Also see the discussion in the text.

Table IV. Shortest Interionic Contacts Involving the Te/Se Anions[a]

contact	compd 1	contact	compd 2
Te···H1151′	3.49	Te···H226A	3.32
Te···H1152′	3.41	Te···H220A^{i}	3.38
Te···H222″	3.56	Te···H15A^{ii}	3.54
Se1···H1262‴	2.90	Te···H226B	3.54
		Se1···N2s^{iii}	3.83 (5)
Se1···H2121^{iv}	2.93	Se1···H13A^{ii}	3.22
Se1···H2191″	3.29	Se1···H126B^{iv}	2.99
Se2···N1s^{v}	3.49 (2)	Se1···H23A^{v}	2.94
Se2···H161^{v}	3.35	Se2···N1S^{vi}	3.67 (4)
Se2···H1152′	3.37	Se2···H122B^{viii}	3.28
Se2···H1231^{iv}	3.30	Se2···H123A^{vii}	3.26
Se2···H262^{vi}	3.38	Se3···N2S^{iii}	3.63 (5)
Se2···H2232′	3.30	Se3···H115A^{viii}	3.36
		Se3···H117B^{viii}	3.19
N1s,N2s···H	>3.06	Se3···H215B^{iii}	3.34
		Se3···H217A^{iii}	3.13

[a] Typical van der Waals sums are as follows: Te + N = 3.7 Å, Se + N = 3.5 Å, Te + H = 3.3–3.5 Å, and Se + He = 3.1–3.3 Å. Te–Se1···H1262 = 165°; Te–Se1···H2121 = 120°.

In the V-shaped $TeSe_2^{2-}$ anion, the Te–Se bond lengths correspond to an average bond order of ca. 1.11 obtained by using eq 1. A similar shortening of the Te–Te bond lengths in examples of the Te_3^{2-} anion relative to α-Te has been observed,[2] and in other longer Ch_n^{2-} ($n \geq 4$) anions, it has been observed that the Ch_{term}–Ch_{bridge} bonds are ca. 0.02–0.04 Å shorter relative to the adjacent Ch_{bridge}–Ch_{bridge} bonds when the countercation is large and nonpolarizable.[2-10] The magnitude of this difference is a function of the dihedral angle involving the central bond[20] (a measure of the eclipsing of lone and bonding pairs), and its effects often propagate to give a short–long–short... bond length alternation in the largest anions and corresponding neutral species. Although this bond length difference could be taken as evidence for multiple bonding for the $TeSe_2^{2-}$ anion, the degree of π character relative to the selenotellurite anion is quite small (bond order ≈ 1.1).

Interestingly, the Se–Te–Se bond angles in $TeSe_2^{2-}$ (111.3 (1)°) and the Te–Te–Te angles in the Te_3^{2-} anion [113.1, 105.7, and 110.9–112.2° in 2,2,2-crypt-K^+ and $Ba(en)_x^{2+}$ salts but 100.1–109.4° in intermetallics with K^+, Rb^+, Cs^+ and Ba^{2+}]^2 are usually larger than the maximum bond angle of 109.5° predicted by the VSEPR rules for two bond pairs and two lone pairs around an atom. Furthermore, in a recent study on the trichalcogenide anions $TeSe_nTe_{2-n}^{2-}$ (n = 0–2), we have found unusually large spin–spin coupling constants for the anions.[14] In order to account for these observations, a bonding model was proposed for the Ch_{term}–Ch_{bridge} bonds in which the atomic hybrid of Ch_{bridge} used in the bond had a relatively large s character. As the σ Ch_{term}–Ch_{bridge} bond would now be polarized toward Ch_{bridge}, owing to its increased electronegativity, the negative charge of Ch_{term} is partially delocalized. In general, it has been observed for a large number of molecules that the bond distances become shorter with increasing s character of the bonds.[21] The shortening of the Ch_{term}–Ch_{bridge} bonds of the polychalcogenide anions can therefore be rationalized as arising from the increased s character of the atomic hybrid of the Ch_{bridge} atoms in the bonds.

Notably, the average Te–S bond length in the thiotellurite anion TeS_3^{2-} in a barium salt (2.358 Å)[16] is only marginally longer (by 0.03 Å) than the average Te–Se distance in the isostructural $TeSe_3^{2-}$ anion when the difference in the covalent radii of S and Se of 0.13 Å is taken into account. Furthermore, the average Se–Te–Se bond angle in $TeSe_3^{2-}$ of 107.0 (17)° is somewhat larger than the S–Te–S bond angles observed for the TeS_3^{2-} anions in the above Ba^{2+} salt [100.5 (2)° × 2; 101.2 (4)°][16] and the TeS_3^{2-} anions in the salts $(NH_4)_2TeS_3$,[15] $BaTeS_3{\cdot}2H_2O$,[15] and $K_3(SH)TeS_3^{2-}$,[17] where S–Te–S angles range from 99.3 to 105.3° with the one exception of 111.3°. According to VSEPR rules, this might signify that sulfur is more electronegative than selenium in these TeX_3^{2-} systems. However, the comparison of these small bond length and bond angle differences between $TeSe_3^{2-}$ and TeS_3^{2-} is made difficult by the large variations in S–Te–S bond angles in the latter due to the geometries of these anions being significantly affected by their crystal environments. Thus, in the TeS_3^{2-} systems and for the TeS_3^{2-} anions in the Na^+ and K^+ salts, additional Te···S and Te···Se contacts or secondary bonds are observed (cf. ref 13 and 16) while in the present salt the bulky crypt ligands prevent any interactions between the $TeSe_3^{2-}$ anions. Instead, contacts involving hydrogen atoms in the 2,2,2-crypt and en molecules are observed (Table IV).

Compounds 3 and 4 contain mixtures of Te–Se anions, and a population analysis of the six partial atom sites in the vicinity of the anion is given in Table III, although the errors presented for the compositions should be regarded as somewhat conservative. However, no constraints on the population parameters were introduced in the least-squares refinements. Although these values are obviously correlated with thermal parameters etc., the ca. 5% decrease in the % Te, and the concomitant increase in population parameters (ca. 7%) at the Se(5) and especially Se(4) sites (which presumably must result from a chain $Te_xSe_y^{2-}$ anion with all compositions except $TeSe_3^{2-}$, an interpretation most consistent with the NMR data reported in ref 14), the internally consistent agreement between the two refinements is reassuring. Also, if the disorder arises from pyramidal and chain anions, then the sum

---

(20) Hordvik, A. *Acta Chem. Scand.* **1966**, *20*, 1885.

(21) Bent, H. A. *Chem. Rev.* **1961**, *61*, 275.

of the population parameters (pp) for the Se(2) and Se(5) sites should be close to 1.0. (This assumes that the predominant orientation of the minor constituent chain anion would involve the trans-related *sites* Se(3)–Se(5)–Se(1)–Se(4) as is likely). The observed sums are the same (1.054) in the two data sets and again reassuringly consistent trends between the pp's of the two sites are observable.

Overall, the anion composition in the two compounds is essentially $Te_{0.9}Se_{3.4}^{2-}$, assuming that the sites labeled Te(1), Se(1), and Se(3) represent admixtures of Te and Se only, although summation of the total number of electrons at all six sites (158.1 in **3** and 160.1 in **4**) is slightly in excess of the total expected for a composition $TeSe_3^{2-}$ (156 electrons). The likely position of the Te atom(s) in the minor component chain dianion is uncertain as disordered arrangements are highly likely. However, the population parameters (pp's) of the Se(1) and Se(3) sites are consistently higher in **4** than those in **3** where, judging from the pp's of the Te(1) and Se(4) sites, there should be more of the chain dianion. Equivalently, an estimate of the pyramidal:chain $TeSe_3^{2-}$ composition can be arrived at by averaging the pp's of the Te(1) and Se(2) sites. Thus, compound **3** consists of 88.5% (11.5%) of the pyramidal (chain) anions while the ratio in **4** is 81.5% (19.5%). Perhaps somewhat fortuitously, the sum of the number of electrons at the remaining four sites in the two compounds is then 9.5% higher in **4** than **3** (89.8/82.0). Although bond lengths and bond angles (Table II) vary over a wide range, especially for the minor constituent atoms, it is notable that the long Se1⋯Se5 separations (2.90 and 2.91 Å) are consistent with the NMR observation that only chain anions in solution have central Te–Te bonds. Additionally, the average Te–Se bond length (2.47 Å; range of values 2.420–2.562 Å) and Se–Te–Se bond angle (108.5°; range of values 104.8–110.9°] for the major pyramidal anion atoms are reasonably close to the values in the other example above (2.460 Å and 107.0°) (Figure 2).

Observation of disordered mixed anions in structures obtained from systems involving Na^+ and K^+ 2,2,2-cryptand counterions or ethylenediamine has been observed before, notably, in a 2,2,2-crypt-K^+ structure involving the heteropolyatomic anions $TlSn_9^{3-}$ and $TlSn_8^{3-}$ occupying the same anion site,[22] and another Zintl type structure has appeared with puzzling residual electron density features around the two Te_3^{2-} ligands that constitute part of the structure of a n-Bu_4N^+ salt of a $Hg_4Te_{12}^{4-}$ anion.[23]

The crystal packings in compounds **1**, **2**, and **4** are indicated in the supplementary figures. Both **2** and **3** (**4**) form layered structures and there is an approximate relationship between the two packing arrangements since the unit cells are related by $a_3 \approx a_2$, $b_3 \approx a_2 + 2c_2$, and $c_3 \approx 2/3\ c_2$. Selected interionic contacts are given in Table IV. In **1** the shortest contact is Se2⋯N1s^v at 3.49 (2) Å compared with Se⋯N solvent contacts >3.6 Å in **2**, while the other Se atom in the $TeSe_2^{2-}$ anion in **1** is involved in two weak Se⋯H contacts of ca. 2.9 Å. This hydrogen bond also has a constraining effect on the temperature factor of the Se atom involved [B_{eq}(Se(2)) = 0.0473 (2) Å^2; cf. B_{eq} = 0.0648 (3) Å^2 for Se(1)]. For comparison, a Te⋯H–O hydrogen bond has been postulated with a Te⋯O distance of 3.585 (7) Å and a Te⋯H–O angle of 172° in $(Ph_4P^+)_2Te_4{\cdot}CH_3OH$, the shortest Te⋯N contact in $(2,2,2\text{-crypt-K})_2Te_3{\cdot}en$ is 3.46 (6) Å, and Se⋯O hydrogen bond distances for the compound $Na_2GeSe_4{\cdot}14H_2O$ mentioned in ref 24 are in the range 3.361–3.534 (9) Å.

^{77}Se and ^{125}Te NMR Spectroscopy of the Selenothiotellurite Anions, $TeS_mSe_{3-m}^{2-}$ (m = 0–3). For the $TeS_mSe_{3-m}^{2-}$ anions, samples rich in either S or Se were prepared in en in the presence of 2,2,2-crypt, and the corresponding ^{125}Te and ^{77}Se NMR spectra of both solutions were recorded. As expected for a mixture of $TeS_mSe_{3-m}^{2-}$ anions in solution, a total of four ^{125}Te and three ^{77}Se environments were observed (Figure 3 and Table V). Each ^{77}Se and ^{125}Te environment could be identified by comparison of the magnitudes of the satellite doublet spacings arising from the one-bond scalar couplings $^1J(^{77}Se{-}^{125}Te)$. The number of Se and Te atoms in each anion could be determined by comparing the measured satellite peak:central peak area ratio for each environment with the theoretical ratio. The assignment of the ^{125}Te environment of TeS_3^{2-} was based on the absence of satellite doublets and the fact that there is a linear increase in the ^{125}Te chemical shifts for the anions as a function of the number of sulfur atoms in the $TeS_mSe_{3-m}^{2-}$ anions, indicating a homologous series of anions. Moreover, similar to previous studies for the metal chalcogen $HgCh_2^{2-}$, $SnCh_3^{2-}$, $SnCh_4^{4-}$, and $TlCh_3^{3-}$ anions[25] and

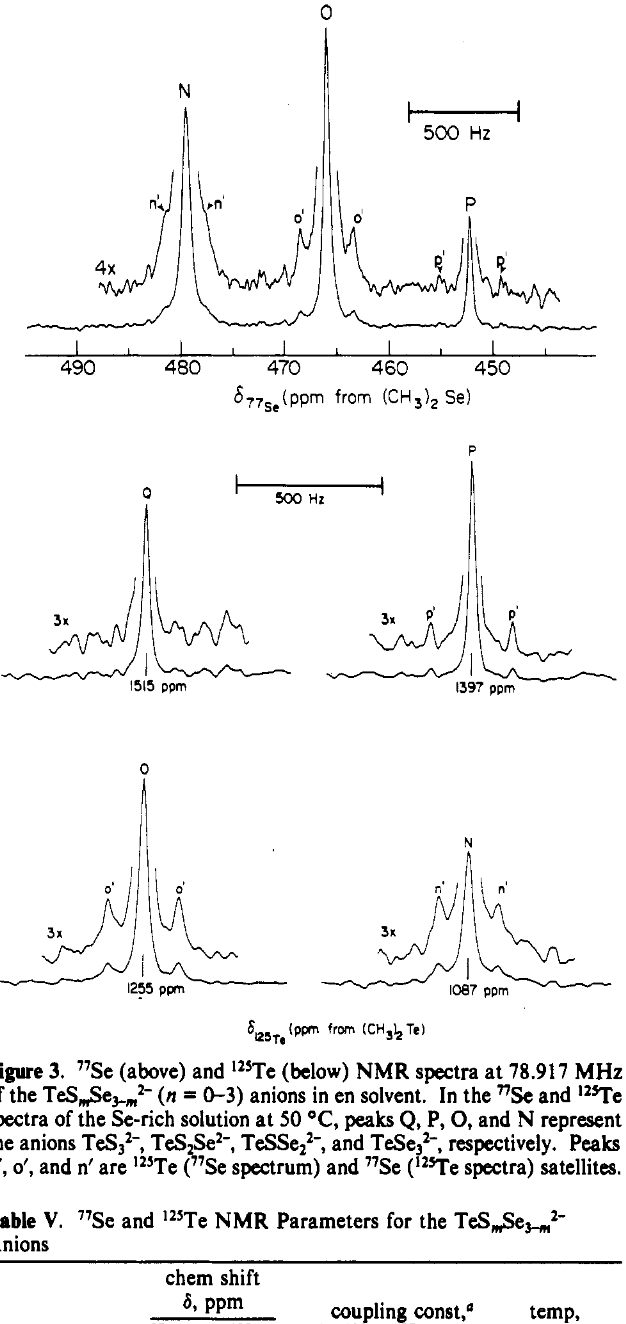


Figure 3. ^{77}Se (above) and ^{125}Te (below) NMR spectra at 78.917 MHz of the $TeS_mSe_{3-m}^{2-}$ (n = 0–3) anions in en solvent. In the ^{77}Se and ^{125}Te spectra of the Se-rich solution at 50 °C, peaks Q, P, O, and N represent the anions TeS_3^{2-}, TeS_2Se^{2-}, $TeSSe_2^{2-}$, and $TeSe_3^{2-}$, respectively. Peaks p′, o′, and n′ are ^{125}Te (^{77}Se spectrum) and ^{77}Se (^{125}Te spectra) satellites.

Table V. ^{77}Se and ^{125}Te NMR Parameters for the $TeS_mSe_{3-m}^{2-}$ Anions

anion	chem shift δ, ppm ^{77}Se	chem shift δ, ppm ^{125}Te	coupling const,[a] $^1J(^{125}Te{-}^{77}Se)$, Hz	temp, °C
$TeSe_3^{2-}$		1087		24
	480		210 (29.0, 17.4)	50
$TeSSe_2^{2-}$		1255		24
	466		244 (33.7, 20.3)	50
TeS_2Se^{2-}		1396		24
	452		288 (39.8, 23.9)	50
TeS_3^{2-}		1514		24

[a] Estimated experimental error in J couplings is ±6 Hz. ^1K(Te–Se) and $^1K_{RC}$(Te–Se) are given in parentheses in units of 10^{20} N A^{-2} m^{-3}. Calculations of reduced coupling constants (^nK) and relativistically corrected reduced coupling constants ($^nK_{RC}$) are discussed in ref 25.

---

(22) Burns, R. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 2804.
(23) Haushalter, R. C. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 433.
(24) Krebs, B.; Jacobsen, H. *Z. Anorg. Allg. Chem.* **1982**, *421*, 97.

the $Pb_2Ch_3^{2-}$ anions[26] (Ch = Se and/or Te), the ^{125}Te and ^{77}Se chemical shifts and the one-bond coupling constant, $^1J(^{125}Te-^{77}Se)$, vary almost linearly with the number of S atoms in the series $TeS_mSe_{3-m}^{2-}$.

The ^{77}Se chemical shifts of the $TeS_mSe_{3-m}^{2-}$ anions are found to be at much higher frequencies than the corresponding selenium environments of the $Se_{term}-Te_{bridge}$ units of the open-chain tri- and tetrachalcogenide anions.[14] In general, the chemical shifts of the heavier elements are believed to be dominated by the paramagnetic term, σ^p, in Ramsey's shielding expression.[27]

$$\sigma = \sigma^d + \sigma^p \qquad (2)$$

This trend could be caused by an increase in the electron unbalance, P_u, for Se, thereby increasing the paramagnetic chemical shift, as it is now bonded to a more electronegative Te atom.[28] A similar trend in which the ^{77}Se chemical shift increases with the higher electronegativity of a substituent directly bonded to selenium has previously been noted.[29] The π character of the Se–Te bonds in $TeCh_3^{2-}$ anions should also result in greater deshielding as is observed for ^{77}Se in selenoketones.[30]

The ^{77}Se chemical shifts become more shielded as the number of sulfur atoms increases in the $TeS_mSe_{3-m}^{2-}$ series. A similar increase in the shielding of both the ^{77}Se and the ^{125}Te chemical shifts as a function of the number of Se atoms is observed for the $TlCh_3^{3-}$, $SnCh_3^{2-}$, and $SnCh_4^{4-}$ anions (Ch = Se and/or Te). A small but significant π back-bonding is expected from the Ch atoms to the central metal atoms for these anions. McFarlane et al.[31] have rationalized the observed increase in ^{77}Se chemical shielding of organophosphorus selenides, R_3PSe, having π-donating groups, R, as arising from a decrease in the contribution of the formal $d\pi-p\pi$ bond between phosphorus and selenium. By analogy, the observed trends for the terminal chalcogenide chemical shifts in the $TeS_mSe_{3-m}^{2-}$, $TlCh_3^{2-}$, $SnCh_3^{2-}$, and $SnCh_4^{4-}$ anions can be accounted for by considering the following order of π-donating strength; $\pi(S\rightarrow) > \pi(Se\rightarrow) > \pi(Te\rightarrow)$. The relatively large change in the ^{125}Te chemical shifts upon substitution of S for Se is somewhat unusual if one considers only the electronegativity difference between S and Se. However, increasing participation of the d orbitals of Te in the sulfur-rich anions can lead to higher deshielding for ^{125}Te owing to an additional term in the paramagnetic chemical shift, σ^p, for tellurium as given by eq 3 where μ_0 is the permeability constant, h is Planck's

$$\sigma^p = \frac{-\mu_0 e^2 h^2}{6\pi m^2 \Delta E}[\langle r^{-3}\rangle_{5p}P_u + \langle r^{-3}\rangle_{5d}D_u] \qquad (3)$$

constant, m is the electron mass, ΔE is the average excitation energy, $\langle r^{-3}\rangle_{5p}$ and $\langle r^{-3}\rangle_{5d}$ are the inverse cube expectation values for the 5p and 5d electrons, respectively, and P_u and D_u are the p and d electron imbalances, respectively. Thus, as the number of the stronger Te–S π bonds increases for the $TeS_mSe_{3-m}^{2-}$ anions, the d-electron imbalance of Te correspondingly increases.

In general, the magnitude of the one-bond coupling constant, $^1J(A-B)$, increases as the substituents bonded to atom A become more electronegative.[32] This has been rationalized as being due to the increased s character of the A–B bond as the effective electronegativity of A increases when the spin–spin coupling is dominated by the Fermi contact mechanism. Interestingly, the values of $^1J(^{125}Te-^{77}Se)$ for the $TeSe_mSe_{3-m}^{2-}$ anions increase with m, indicating that S is more electronegative than Se. However, the relatively small values of $^1J(^{125}Te-^{77}Se)$ for the $TeS_mSe_{3-m}^{2-}$ anions could arise from approximately equal but opposite contributions of different excitations in the Fermi contact interaction.[33] Therefore, the true trend could be opposite to the one above and similar to that found for the small coupling constants of $Pb_2Se_nTe_{3-n}^{2-}$ anions.[26]

Although the electronegativity order $\chi_S > \chi_{Se}$ cannot be determined with certainty from trends in a single parameter, additional evidence from the relative bond angles of $TeSe_3^{2-}$ and TeS_3^{2-} does appear to indicate that sulfur is more electronegative than selenium in this series of $TeS_mSe_{3-m}^{2-}$ anions.

Experimental Section

Preparation of Heterotri- and -tetrachalcogenide Anions. Details outlining the apparatus used in preparing and handling these materials and related materials are given in refs 14 and 25.

The desired stoichiometric amounts of K_2Te and chalcogen powder were thoroughly mixed in a glass ampule. For most of the preparations, and particularly those involving K_2Te, the 2,2,2-crypt was not added to the solution until all of the monochalcogenide had reacted in order to prevent the possibility of oxidizing the monochalcogenide. The KTe_2 phase was prepared in thick-walled Pyrex glass vessels by a procedure similar to that described in ref 14. The amount of 2,2,2-crypt used was usually kept in 3–6% excess relative to the total amount of alkali metal in order to ensure that all the alkali-metal cations were complexed in solution. In order to compensate for the possibility that small amounts of the polychalcogen anions may be oxidized in solution, the monochalcogenides were always in 2–5% excess relative to the chalcogen metals. After approximately 10 mL of en had been vacuum distilled onto the mixture at 0 °C, the solutions immediately became colored. The solutions were allowed to react for a further 1–3 days at room temperature before they were cooled in an ice bath, and a stoichiometric amount of 2,2,2-crypt was decanted in small portions into the solutions.

Samples for NMR studies were prepared by allowing the undissolved materials to settle prior to decantation of the clear solutions into precision thin-walled 10-mm-o.d. NMR tubes attached to the reaction vessels. The solutions were concentrated to 2–4 mL as described in ref 25. The concentrations of the anions in the NMR samples often times could not be specified owing to large amounts of crystalline solid formation upon concentration of the NMR sample solutions. When crystal formation occurred, the material was collected into the top of the sealed inverted glass NMR tube. After NMR analysis, the crystals were isolated in an inert-atmosphere glovebox and dried under dynamic vacuum prior to being transferred and sealed in Lindemann tubes for single-crystal X-ray structure determination (see below).

In typical preparations of the $TeSe_2^{2-}$ and $TeSe_3^{2-}$ anions in en solvent, the following amounts of reagents were used: for $TeSe_2^{2-}$, K_2Te (63.0 mg, 0.306 mmol), Se (50.1 mg, 0.634 mmol), and 2,2,2-crypt (252 mg, 0.669 mmol); for $TeSe_3^{2-}$, K_2Te (52.3 mg, 0.254 mmol) and Se (60.6 mg, 0.767 mmol). Solutions of $TeSe_3^{2-}$ prepared in this manner were relatively free of other chalcogenide species as demonstrated by NMR spectroscopy. However, small amounts of $TeSe_3^{2-}$ were always present in $TeSe_2^{2-}$ solutions (see ref 14 for NMR studies of these solutions).

The preparation of $TeS_mSe_{3-4}m^{2-}$ (m = 0–3) anions in en was conducted in a similar way. The method for the preparation of samples suitable for ^{125}Te and ^{77}Se NMR spectroscopy has been described in detail elsewhere.[25] NMR samples were prepared by allowing K_2Te to react with a 2:1 S–Se mixture and a 1:2 S–Se mixture in en followed by the addition of stoichiometric amounts of 2,2,2-crypt (130–150 mg). The resulting solutions were dark orange-red in color. The details of the acquisition of ^{77}Se and ^{125}Te NMR spectra are given in ref 14.

X-ray Crystallography. Crystals of compounds **1**–**4** were obtained as dark red-brown blocks and plates from en solution (see above) and were sealed in 0.2–0.3 mm Lindemann capillaries in a drybox under nitrogen. All further work on selected crystals was performed on the diffractometer. Details for each compound are summarized in Table VI. For each data set, corrections for Lorentz–polarization, crystal decay (compounds **2** and **3**), and absorption (compounds **2** and **4**—after the composition of each crystal was reasonably well established[34]) were applied to all the

---

(25) Burns, R. C.; Devereux, L. A.; Granger, P.; Schrobilgen, G. J. *Inorg. Chem.* **1985**, *24*, 2615.

(26) Bjőrgvinsson, M.; Sawyer, J. F.; Schrobilgen, G. J. *Inorg. Chem.* **1987**, *26*, 741.

(27) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.

(28) Webb, G. A. In *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 1, Chapter 4, p 79.

(29) Rodger, C.; Sheppard, N.; McFarlane, C.; McFarlane, W. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; Chapter 12, p 411.

(30) Cullen, E. R.; Guziec, F. S.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 7055.

(31) McFarlane, W.; Rycroft, D. S. *J. Chem. Soc.* **1973**, 2162.

(32) Jameson, C. J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press, New York, 1987; Chapter 4.

(33) McFarlane, W. *J. Chem. Soc.* A **1969**, 670.

(34) The crystal of **2** was a truncated pyramid bound by the faces (101), (101), (001), (111), and (011), which were 0.0094, 0.0094, 0.0075, 0.0075, and 0.0075 cm from an origin within the crystal. Calculations using an 8 × 10 × 8 Gaussian grid gave a range of transmissions from 0.570 to 0.835. The crystal of **4** was a plate with broken edge faces, which was described by the forms {001} and {100} and faces (120) and (120), which were 0.0044, 0.0094, 0.0088, and 0.0088 cm from an origin within the crystal. Calculations using a 10 × 10 × 6 grid gave a range of transmissions from 0.666 to 0.800.

Table VI. Crystal Data, Details of Intensity Measurements, and Structural Refinement[a]

	(2,2,2-crypt-K)$_2$TeSe$_2$·en (1)	(2,2,2-crypt-K)$_2$TeSe$_3$·en (2)	(2,2,2-crypt-K)$_2$TeSe$_3$·en (3 + 4)[b]	
system	triclinic	trigonal	monoclinic	
a, Å	10.9725 (8)	12.386 (5)	12.252 (4)	12.286 (2)
b, Å	12.1940 (9)	12.386 (5)	21.643 (3)	21.587 (9)
c, Å	12.3242 (10)	30.669 (15)	20.718 (3)	20.759 (2)
α, deg	59.182 (7)	90	90	90
β, deg	73.781 (7)	90	97.45 (2)	97.61 (1)
γ, deg	67.718 (6)	120	90	90
V, Å	1303	4076	5447	5457
fw	1176.8	1255.8	1255.8	
Z/d, g cm^{-3}	1/1.500	3/1.537	4/1.531	
space group	$P1$ (No. 1)	$P3_2$ (No. 145)[c]	$P2_1/n$ (No. 14)	
μ(Mo Kα), cm^{-1}	21.7	27.5	27.4	
no. of reflcns in cell detmn	25	25	25	25
2θ range, deg	11.2–15.8	8.3–13.1	9.0–14.9	8.7–14.9
scan widths, deg	0.65 + 0.35 tan θ	0.65 + 0.35 tan θ	0.65 + 0.35 tan θ	0.60 + 0.35 tan θ
max scan time, s	65	65	60	55
std. reflcns: no./interval, s	3/7000	3/9000	3/7200	3/7000
max 2θ	55	52	50	48
octants	$h,\pm k,\pm l$	$h,\pm k,\pm l$	$h,k,\pm l$	$h,k,\pm l$
tot. no. of data collcd	7095[d]	8362[e]	10638[f]	9040[f]
no. of std reflcns	189	207	306	237
max decline in intens of std reflcns, %	<±5	−9.0	−9.5	<±4
CHORT[g]				
min cor	NA	0.968	0.970	NA
max cor		1.194	1.202	
no. of syst abs or F_o data rejected	512	1840	2974	1963
no. of sym equiv data merged	0	1738	304	3
$R_{merge}(F)$	0.0	0.087	0.070	0.065
unique data	6394	2304	7054	6919
no. obsd data	4459 [$I \geq 3\sigma(I)$]	1810 [$I \geq 2.5\sigma(I)$]	2150 [$I \geq 3\sigma(I)$]	2898 [$I \geq 3\sigma(I)$]
R (R_w)	0.0382 (0.0465)	0.0574 (0.0638)	0.0733 (0.0730)	0.0667 (0.0632)
max Δ/σ in final cycle of least squares	0.40 (en)	0.07	0.18	0.11
weights, value of p	0.055[g]	0.060[h]	0.00241[i]	0.00030[i]
esdouws	1.23	1.31	NA	NA
max peak final F, e Å^{-3}	1.06 [0.9 Å from Se(1)]	0.63 [1.1 Å from Te(1)]	1.12 [near Te(1) and Se(3)]	0.80 [near Se(1) and Se(2)]

[a] Enraf-Nonius CAD4 diffractometer; Mo Kα (graphite monochromator); λ = 0.71069 Å; T = 298 K for all four compounds; ω–2θ mode; prescans at 10 deg min^{-1}; other scan speeds chosen to give $I/\sigma(I) \geq 25$ within maximum scan time specified; backgrounds, by extending scan by 25% on either side of peak, were measured for half the time taken to collect the peak. [b] TeSe$_3^{2-}$ composition assumed for the anion in calculating fw, d_x, and μ. [c] Systematic absence 000l, $l = 3n$ is consistent with several trigonal and hexagonal space groups (cf. ref 9). See text for discussion of space group determination. [d] Total includes 189 standard reflections and 958 reflections in the octants $-h,\pm k,\pm l$ with $2 \leq 30°$. [e] Reflections from this crystal were somewhat broad and weak leading to several large deviations ($\Delta \leq 0.62°$) between observed and calculated positions of the reflections used in the cell determination. Extra symmetry data were collected to improve the quality of the data set and to aid in the space group determination. [f] 0kl for h = 0. [g] Corrections (on F_o) for crystal decay based on standard reflections; NA = not applied. [h] Weights: $w = 4F^2/\{\sigma^2(I) + (pF^2)^2\}$. [i] Weights: $w = [\sigma^2(F) + pF^2]^{-1}$.

data collected. Each structure was solved and refined by standard methods. For **1**, extra data were available and the correct "hand" was readily established before final refinements with anisotropic C/N/O atoms were attempted for all non-hydrogen atoms except those in the en solvent. In the case of compound **2**, several space groups are consistent with the observed systematic absences—however, the high symmetries 32, 6, and 622 were not apparent in the diffraction data,[35] and the solution was obtained in space group $P3_2$. Refinement in the enantiomorphous space group $P3_1$ gave higher residuals [R (R_w) = 0.0685 (0.0711) and S = 1.31] and was rejected.[35] For the isomorphous compounds **3** and **4**, refinement was initially performed on compound **3**, and an apparent normal structure solution was obtained. Least-squares lowered the residual to just below 10%, which is often considered reasonable for crypt-containing structures. Furthermore, the only suggestions of anything untoward were some slightly high and slightly different temperature factors for the Se atoms of the assumed TeSe$_3^{2-}$ anion as well as a slight residual peak within bonding distance of Se(1), again something that could have been dismissed as being due to the lack of an absorption correction. At this point, slightly different cell parameters and reflection intensities were observed for a second crystal, and on completion and processing of the intensity data from this second crystal, we observed that refinement resulted in even larger residual features in a difference Fourier map (residual peaks of ca. 5 e Å^{-3}). Least-squares refinement of partial atom sites Se(4) bonded to Se(1) and Se(5) near Te with isotropic temperature factors as well as the population parameters of the original four atom sites without any other constraints resulted in substantial improvements in the crystallographic residuals for compound **4** and were readily repeated for compound **3** (see Table III, additional details).

In all four refinements, hydrogen atoms in all of the crypt moieties were placed in calculated positions with common temperature factors. In **1**, the availability of a larger number of observed data allowed anisotropic refinement of the C, N, and O atoms of the two crypt ligands; otherwise, only Te, Se, and K (major Te/Se positions only in the mixed anions in **3** and **4**) were allowed anisotropic displacement amplitudes. Full-matrix (**1** and **2**) or least-squares refinement in large blocks (**3** and **4**) minimizing $\Sigma w \Delta F^2$ then converged to the residuals given in Table VI.

All calculations were performed by using the Enraf-Nonius SDP package[36] and SHELX[37] on PDP11/23 and Gould 9705 computers. Neutral-atom scattering factors in the analytical form were taken from ref 38 or were stored in the program.

---

(35) Thus, in $P6_2$ the R_{merge} index was 0.207 for averaging 6315 reflections down to 2626 with 306 rejected from the calculations as being too dissimilar in intensity from the average. Corresponding values for $P6_222$ (No. 180) were R_{merge} = 0.217 with 336 rejected from the calculations. Similar R values and numbers of rejected data were found for $P3_121$ (No. 152), which produced 3645 reflections in the final data set. Finally in $P3_112$, R_{merge} was 0.098 but 38 reflections were rejected in producing the final data set of 4505 reflections. As a check on the composition of the anion in compound **2**, the population parameters of the Te and Se atoms were allowed to refine (no other constraints), but the least-squares refinement gave no significant variations from 1.0 for these atoms.

(36) *Enraf-Nonius Structure Determination Package*; B.A. Frenz and Associates, Inc.: College Station, TX, 1981.

(37) Sheldrick, G. M. *SHELX Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

Acknowledgments. We thank H. P. Mercier and S. Tsai for their help. The Natural Sciences and Engineering Research Council of Canada is thanked for providing operating grants (G.J.S.) and an equipment grant for the X-ray diffractometer (Chemistry Department, University of Toronto), and McMaster University and the Ontario Ministry of Colleges and Universities for the award of a fellowship and scholarships, respectively, to M.B.

Registry No. **1**, 136236-85-6; **2**, 136236-87-8; K_2Te, 12142-40-4; Se, 7782-49-2; $TeSSe_2^{2-}$, 136202-30-7; TeS_2Se^{2-}, 136202-29-4; TeS_3^{2-}, 12300-21-9; ^{77}Se, 14681-72-2; ^{125}Te, 14390-73-9; $TeSe_3^{2-}$, 133911-10-1.

Supplementary Material Available: Tables of general temperature factor expressions U_{ij}'s for $TeSe_2^{2-}$ in compound **1** and pyramidal $TeSe_3^{2-}$ in compound **2**, bond lengths and bond angles for the 2,2,2-crypt-K^+ cations of compounds **1** and **2**, and positional and thermal parameters and selected bond lengths and bond angles for compounds **3** and **4** and stereoviews showing the packing of $[2,2,2\text{-crypt-K}]_2TeSe_2\cdot en$ (**1**), $[2,2,2\text{-crypt-K}]_2TeSe_3\cdot en$ (**2**), and $[2,2,2\text{-crypt-K}]_2TeSe_3\cdot en$ (**4**) (26 pages); tables of final structure factor amplitudes for compounds **1**–**4** (66 pages). Ordering information is given on any current masthead page.

---

(38) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch: Birmingham, England, 1974; Vol. 4.

Contribution from the Dipartimento di Chimica,
Università di Firenze, Firenze, Italy

Tetracyanoquinodimethane Salts of Transition-Metal Complexes. 2.[1] Single-Crystal Electron Paramagnetic Resonance of Tris(1,10-phenanthroline)zinc(II) Bis(tetracyanoquinodimethanide) and Tris(1,10-phenanthroline)copper(II) Bis(tetracyanoquinodimethanide)

Alessandro Bencini* and Claudia Zanchini

Received February 7, 1991

The single-crystal and polycrystalline powder EPR spectra of the compounds $Zn(phen)_3(TCNQ)_2$ and $Cu(phen)_3(TCNQ)_2$ have been recorded at the X-band frequency in the temperature range 300–4.2 K. In the Zn derivative, a Frankel-type excitonic spectrum was observed attributed to one of the two magnetically nonequivalent $TCNQ^-$ ions seen in the crystal structure. The triplet exciton spectra were interpreted with a dipolar zero field splitting tensor with $|D_1| = 66\ (2) \times 10^{-4}\ cm^{-1}$ and $|E_1/D_1| = 0.12\ (1)$. These values nicely agree with the spin density distribution computed with the Xα–SW method. Less intense features seen in the crystal spectra at temperatures lower than 20 K were assigned to a $S = 2$ state arising from exciton–exciton interactions. The zero field splitting of the $S = 2$ state was measured to be $|D_2| = 35\ (2) \times 10^{-4}\ cm^{-1}$ and $|E_2/D_2| = 0.07\ (1)$. The EPR spectra of $Cu(phen)_3(TCNQ)_2$ showed only resonances due to one unpaired electron localized on a copper(II) center. The spectra have been found to be temperature dependent, the principal g values being $g_x = 2.037\ (3)$, $g_y = 2.052\ (3)$, and $g_z = 2.104\ (3)$ and $g_x = 2.052\ (3)$, $g_y = 2.057\ (3)$, $g_z = 2.180\ (3)$ at 290 and 4.2 K, respectively. This temperature dependence has been attributed to interactions of the copper(II) ion unpaired electron with the mobile triplet excitons of $TCNQ^-$.

Introduction

The number of compounds containing TCNQ (TCNQ = tetracyanoquinodimethane) and related molecules and transition-metal or organometallic complexes is increasing day after day, and most of these solids have shown unusual magnetic and/or charge conduction properties.[2-5] In the majority of these compounds, the nonorganic part plays an important role in determining the arrangement of the TCNQ molecules in the solid and, often, in governing a partial transfer of charge to the TCNQ. Examples of these compounds range from the simple alkali-metal salts of $TCNQ^-$, either containing TCNQ radicals with a 1− charge or more complex systems like $(TCNQ)_3^{2-}$ anions, to solids in which charged clusters of metals crystallize together with TCNQ molecules.[5-10] An incomplete charge transfer to TCNQ often is associated with electrical conduction, while a complete charge transfer is often associated with peculiar magnetic properties such as the formation of mobile triplet excitons.[7-10]

With the aim to investigate the nature of the interactions between the organic radicals and between the organic and the inorganic parts of the solid, we started a research program devoted to the synthesis and structural and magnetic characterization of TCNQ-containing solids having inorganic parts as simple as possible but undergoing some dynamic effect such as Jahn–Teller distortion or valence delocalization. The main purpose for this is to have simpler systems that could be investigated through the largest number of experimental techniques and having some electronic structure, in the inorganic part, that could modulate the interactions between the organic electrons. As a first attempt, we looked for systems undergoing dynamic Jahn–Teller distortions and we synthesized salts of general formula $M(phen)_3(TCNQ)_2$, where M is a bipositive first-row transition-metal ion and phen is the aromatic ligand 1,10-phenanthroline. The stoichiometry of these solids suggests that the charge transfer between the metal and the TCNQ is complete, and therefore TCNQ is present in the −I oxidation state. No significant electric conduction was

---

(1) Part 1: Bencini, A.; Midollini, S.; Zanchini, C. *Inorg. Chem.* **1989**, *28*, 1963.

(2) Miller, J. S.; Epstein, A. J. In *Electron Transfer in Biology and the Solid State*; Johnson, M. K., King, R. B., Kurtz, D. M., Jr., Kutal, C., Norton, M. L., Scott, R. A., Eds.; Advances in Chemistry 226; American Chemical Society: Washington, DC, 1990; p 419.

(3) Miller, J. S.; Calabrese, J. C.; Harlow, R. L.; Dixon, D. A.; Zhang, J. H.; Reiff, W. M.; Chittipedi, S.; Selover, M. A.; Epstein, A. J. *J. Am. Chem. Soc.* **1990**, *112*, 5496.

(4) Ward, M. A.; Fagan, P. J.; Calabrese, J. C.; Johnson, D. C. *J. Am. Chem. Soc.* **1989**, *111*, 1719.

(5) Endres, H. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1983, Vol. 3, p 263.

(6) Zeller, H. R. *Adv. Solid State Phys.* **1973**, *13*, 31.

(7) Nordio, P. L., Soos, Z. G.; McConnell, H. M. *Annu. Rev. Phys. Chem.* **1966**, *17*, 237.

(8) Hatfield, W. E. *NATO Conf. Ser. 6* **1979**, *1*, 1.

(9) Soos, Z. G. *Annu. Rev. Phys. Chem.* **1974**, *25*, 121.

(10) Soos, Z. G.; Bondeson, S. R. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1983, Vol. 3, p 193.

0020-1669/91/1330-4245$02.50/0 © 1991 American Chemical Society