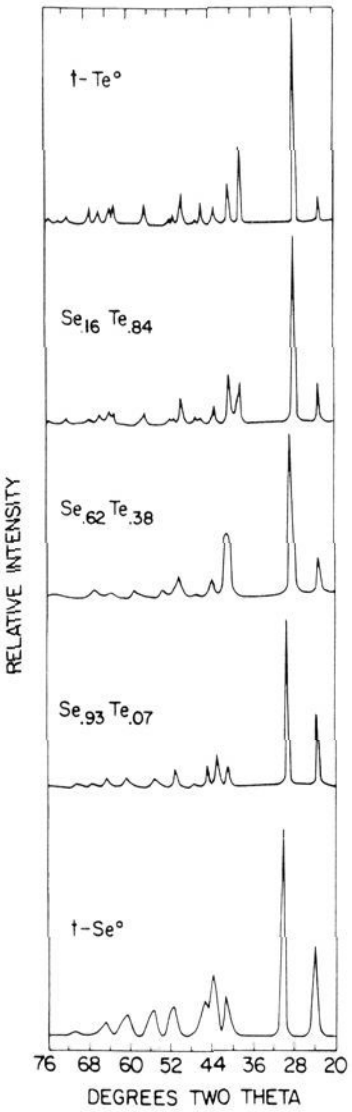

Figure 1. X-ray diffraction spectra (Cu Kα radiation) of precipitated Se_xTe_{1-x} alloy powders.

terpolation of literature values[14-18] for Se–Te alloys of the same composition prepared by conventional melt–quench processes.[18]

Figure 1 shows XRD traces, intensity vs. 2θ, of trigonal Te and trigonal Se along with traces for alloys of composition $Se_{0.1}Te_{0.9}$, $Se_{0.5}Te_{0.5}$, and $Se_{0.9}Te_{0.1}$. The flat base line indicates that the specimens are completely crystalline. It is evident from the absence of splitting, the constant full widths at half-maximum (fwhm), and the well-defined peaks that the materials are single phased. Although the fwhm remains constant for the peaks in each sample, this value differs among the various powders due to differences in average crystallite size. If one looks closely at the intense peak in trigonal Te at 28° 2θ, it can be seen that the position of this reflection gradually moves to larger angle as the mole fraction of Se in the alloy is increased. This shift is in keeping with the different lattice parameters of trigonal Te and trigonal Se.

The homogeneity of the composition of the crystalline alloys was demonstrated by energy-dispersive X-ray analysis (EDXA), wherein diffraction patterns were sampled from various ~1-μm regions of the samples. Scanning electron micrographs (Figure 2a–d) show that the gross morphology of the crystals changes significantly with composition going from rod-shaped faceted crystals at $Se_{0.93}Te_{0.07}$ to faceted-spheroidal crystals at $Se_{0.41}Te_{0.59}$ and back to rod-like crystals at $Se_{0.16}Te_{0.84}$. In light of the common trigonal unit cell evidenced in the XRD, it is surprising to see such dramatic variations in the morphology of the precipitated crystals of different composition.

It has thus been demonstrated that homogeneous crystalline alloys of Se and Te can be prepared by coreduction of solutions of Se^{IV} and Te^{IV} esters. The composition of the alloys mirrors the mole ratio of the esters in solution prior to reduction. The crystalline alloys thus formed exhibit diffraction patterns analogous

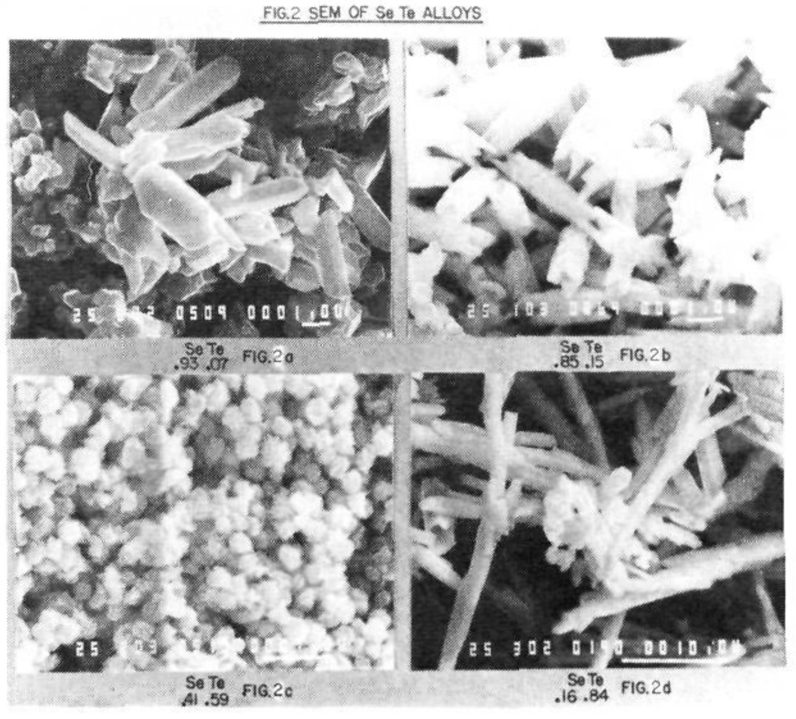

Figure 2.

to those obtained by annealing Se and Te alloyed in the melt.[19,20] There may be subtle structural differences that will manifest themselves in the electronic properties of these materials and such structural differences might be probed by vibrational spectroscopy.[21]

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Registry No. SeO_2, 7446-08-4; TeO_2, 7446-07-3; diethyl selenite, 14364-97-7.

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Recognition of a Semibridging Carbonyl Group in $Mn_2(CO)_9$ from Plane-Polarized Photolysis of $Mn_2(CO)_{10}$ in Ar Matrices at 12 K

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Photolysis of $Mn_2(CO)_{10}$ has long been acknowledged to proceed via homolytic cleavage of the Mn–Mn bond, producing $Mn(CO)_5$ radicals.[1] Later studies[2] also suggested the participation of nonradical species $Mn_2(CO)_n$, where $n = 9$ or 8. These were initially considered to arise by thermal ejection of CO from $Mn(CO)_5$,[2c] but recent work by Yesaka et al.[3] has shown these species to arise from an alternative decomposition of $Mn_2(CO)_{10}$.

When $Mn_2(CO)_{10}$ is photolyzed in an alkane matrix at 77 K, the sole process discernible is the photoejection of CO.[4] This is probably so because the alternative route results only in the im-

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Scheme I

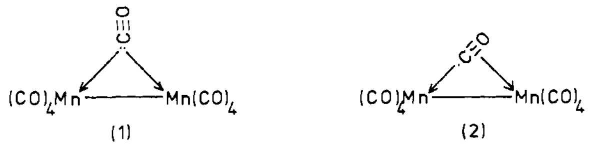

Table I. IR Dichroism Arising from Polarized Partial Photolysis ($\lambda = 296 \pm 5$ nm) of $Mn_2(CO)_{10}$ in Ar at 12 K

species	$\bar{\nu}$/cm^{-1}	dichroism[a]
$Mn_2(CO)_{10}$	2050	∥
	2026	⊥
	2019	⊥
	2009	⊥
	1986	∥
$Mn_2(CO)_9$	2058	∥
	2037	∥
	1993	⊥
	1977	⊥
	1764	0

[a] The terms parallel (∥) and perpendicular (⊥) as used here are defined relative to the peak absorbance polarized parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the photolyzing plane of polarization such that ∥ denotes $A_\parallel < A_\perp$ and ⊥ denotes $A_\parallel > A_\perp$.

mediate cage recombination of $Mn(CO)_5$ radicals. Using these conditions, Hepp and Wrighton were able to record the IR spectrum of $Mn_2(CO)_9$, and they concluded from a band at 1760 cm^{-1} that the molecule contained a bridging carbonyl group. The IR spectrum of $Mn_2(CO)_9$ has also recently been observed as a transient signal following the flash photolysis of $Mn_2(CO)_{10}$.[5]

The structure of $Mn_2(CO)_9$ could be rationalized as containing either a ketonic bridging (**1**) or a semibridging (**2**) carbonyl group. A frequency observation alone is not adequate for determining the actual nature of this group; some form of bond directional determination would also be required. The technique of polarized photochemistry can provide such information[6] and is therefore appropriate for resolving this issue. We now wish to report our results from such a study, which lead to the conclusion that $Mn_2(CO)_9$ contains a semibridging carbonyl group (Scheme I).

Matrices of $Mn_2(CO)_{10}$ were prepared by sublimation from a side arm and deposition on a CsI window at 20 K, with simultaneous condensation of a large excess of argon. The samples were subsequently cooled to 12 K before being partially photolyzed with plane-polarized monochromatic radiation ($\lambda = 296 \pm 5$ nm).[7] This produced a matrix containing an array of $Mn_2(CO)_{10}$ molecules with a linearly dichroic IR spectrum (Table I). The observed dichroism agreed with the accepted peak assignments of $Mn_2(CO)_{10}$[8] and confirmed previous claims, including some based on polarized irradiation of $Mn_2(CO)_{10}$ in pure CO matrices, that the photoactive transition dipole lay along the Mn–Mn σ-bond.[9] The latter was apparent from the nature of the dichroism in the $S^{(b_2)}$ axial modes (2050 and 1986 cm^{-1}). This irradiation also resulted in the generation of a linearly dichroic $Mn_2(CO)_9$ sample. Spectra from this showed the terminal carbonyl peaks to be substantially dichroic, whereas the 1764-cm^{-1} band was devoid of any detectable dichroism[10] (Figure 1 and Table I). If we assume, as is wholly reasonable for such a large molecule, that the Mn–Mn bond direction remains unchanged on ejection of CO, these results could indicate that the group corresponding to the 1764-cm^{-1} band is fluxional or in some other way incapable of supporting dichroism. This, however, was shown to be untrue by further results (vide infra). An alternative explanation is that the band has an associated transition dipole oriented approximately 45° from the photoactive transition dipole of $Mn_2(CO)_{10}$. This would also result in its exhibiting no dichroism on photogeneration of $Mn_2(CO)_9$ from $Mn_2(CO)_{10}$. The most plausible structure consistent with these observations, and the band frequency, is one containing a semibridging carbonyl group (**2**). Such a species has previously been found to contain a metal–metal–CO bond angle of the order of 45° and to exhibit a very low frequency carbonyl stretch.[11] On fundamental grounds, such a four-electron-donating carbonyl would ensure for this molecule the 36-electron configuration required of a stable binuclear metal carbonyl structure.

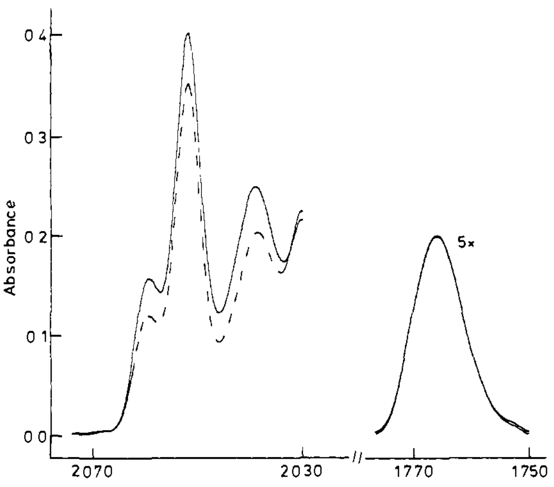

Figure 1. $Mn_2(CO)_{10}$ in Ar at 12 K partially photolyzed with polarized radiation ($\lambda = 296 \pm 5$ nm) for 350 min. Polarized spectra recorded with planes parallel (---) and perpendicular (—) to be the photolyzing plane of polarization.

Altering the conditions of irradiation to wide-band photolysis caused the $Mn_2(CO)_9$ to react. This was seen to occur in two ways. Prolonged wide-band irradiation ($\lambda > 300$ nm) created a new species, recognized by the growth of a band at 2068 cm^{-1}. This was considered to arise from the photoejection of at least one more CO to produce a secondary fragment. The alternative process, induced by $\lambda > 300$ nm radiation, was the photoincorporation of CO to regenerate $Mn_2(CO)_{10}$.

Stimulation of the photoreincorporation of CO into $Mn_2(CO)_9$ by polarized radiation resulted in the formation of dichroic arrays of $Mn_2(CO)_9$ and $Mn_2(CO)_{10}$. The spectra from this process show the 1764-cm^{-1} band to be substantially dichroic, proving this group capable of supporting dichroism. They also show all other bands to exhibit dichroism of an identical nature with that produced by the reaction in the opposite direction. Both of these facts require the photoactive transition dipole of $Mn_2(CO)_9$ to be substantially removed from that of $Mn_2(CO)_{10}$.

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Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Mn_2(CO)9$, 86728-79-2.

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(7) The matrix window was cooled by means of an Air Products Displex Model CSA-202. IR spectra were recorded on a Perkin-Elmer PE684 spectrometer interfaced to a Perkin-Elmer Model 3600 Data Station. The spectrometer was calibrated with a polystyrene film and quoted frequencies are accurate to ±2 cm^{-1}. Polarization of the sample beam was achieved by means of a SpecAc aluminum-grid polarizer on a KRS-5 substrate. The photolysis source was a 200-W high-pressure Hg arc, fitted with a water filter and Polacoat 105 UV WMR polarizer on a quartz substrate. Argon was obtained from B.O.C. Ltd. (Research Grade).

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(10) We estimate that, were the transition moment of this band exactly perpendicular to the photoactive transition of the $Mn_2(CO)_{10}$, then the expected difference between $A_\parallel$ and $A_\perp$ would be about 10 times the signal/noise ratio.

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