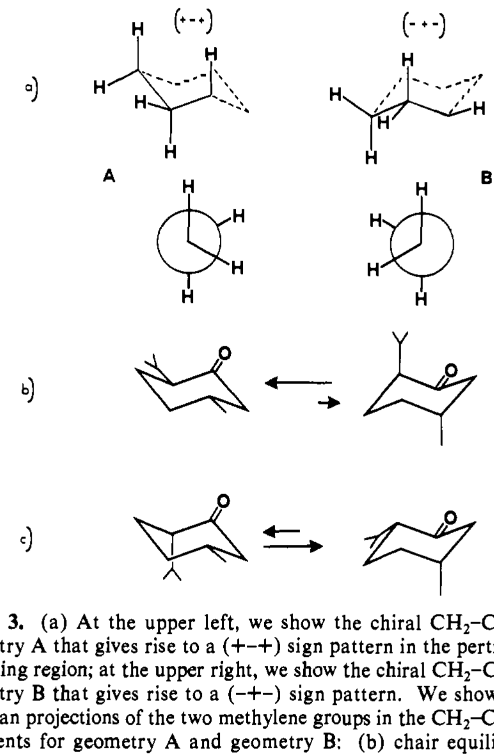

Figure 3. (a) At the upper left, we show the chiral CH_2–CH_2–C*H geometry A that gives rise to a (+–+) sign pattern in the pertinent CH stretching region; at the upper right, we show the chiral CH_2–CH_2–C*H geometry B that gives rise to a (–+–) sign pattern. We show also the Newman projections of the two methylene groups in the CH_2–CH_2–C*H fragments for geometry A and geometry B: (b) chair equilibrium in (–)-menthone; (c) chair equilibrium in (+)-isomethone.

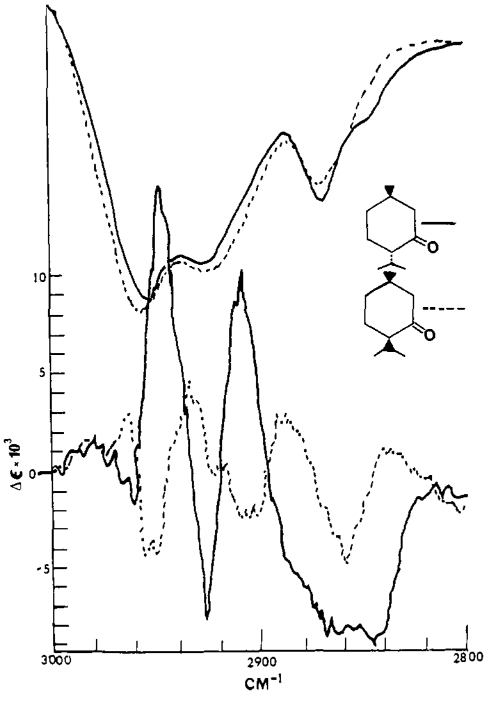

Figure 4. VCD (lower traces) and transmission spectra (upper traces) between 3000 and 2800 cm^{-1} of (–)-menthone (—), 0.059 M in CCl_4, and (+)-isomenthone (---), 0.062 M in CCl_4.

in the disposition of the methine CH bond relative to the methylene CH bonds in the two instances. Nevertheless, on both empirical and computational grounds,[7] the deviations from a strict mirror-image geometrical relationship are not sufficient to spoil the enantiomeric-like relationship between the two sign patterns, i.e., (+–+) for geometry A vs. (–+–) for geometry B.

In Table I we also give the patterns predicted on the basis of the known absolute configuration of the compounds listed. In cases where there would be significant conformational mobility, prior knowledge of the absolute configuration allows one to assign the dominant conformer. This is the situation for (–)-menthone and (+)-isomenthone, whose oppositely signed VCD spectral patterns, shown in Figure 4, are indicative of the dominant conformers indicated in Figure 3b,c.

We have not yet encountered any exceptions to the stated correlation of VCD sign patterns with the chiral sense of the CH_2–CH_2–C*H fragment. Nevertheless, we do call attention to a caveat that carriers over, mutatis mutandis, from the analogous stereochemical analysis of electronic CD data: the isolated nature of the chromophoric transitions must not be destroyed through coupling with other vibrational modes or through the accidental overlapping of the relevant chromophoric CD pattern by other CD bands.[8]

Acknowledgment. We gratefully acknowledge financial support for this research from grants provided by the National Science Foundation (CHE 76-08759 (D.A.L.) and CHE 80-09240 (A. M.)) and the National Institutes of Health (HL-16833 (A.M.)). We also thank Dr. Harry S. Mosher for his valuable contributions to the course of this work.

Registry No. (*R*)-(+)-3-Methylcyclohexanone, 13368-65-5; (*R*)-(+)-3-methylcyclohexanone-2,2,6,6-d_4, 82209-32-3; (*R*)-(+)-3-*tert*-butylcyclohexanone, 72029-73-3; (*R*)-3-*tert*-butylcyclohexanone-2,2,6,6-d_4, 82209-33-4; (–)-menthone, 14073-97-3; (+)-isomenthone, 18309-28-9; (+)-limonene, 5989-27-5; (+)-*p*-menth-1-ene, 1195-31-9; (+)-*p*-menth-1-en-9-ol, 13835-75-1; (–)-β-pinene, 18172-67-3; (–)-*cis*-myrtanylamine, 73522-42-6; (+)-pulegone, 89-82-7; (–)-menthol, 2216-51-5; (–)-perillyl alcohol, 18457-55-1.

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(8) Lightner, D. A.; Bouman, T. D.; Gawroński, J. K.; Gawrońska, K.; Chappuis, J. L.; Crist, B. V.; Hansen, A. E. *J. Am. Chem. Soc.* **1981**, *103*, 5314–5327.

Transition-Metal-Promoted Carbon–Carbon Bond Formation by Reductive Dimerization of Carbon Disulfide: Direct Synthesis of the Bis(1,2-dithiolene-like) Tetrathiooxalato (C_2S_4) Ligand from Carbon Disulfide by Reaction with the Dimeric Nickel(I) Complexes $Ni_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_2$ (R = H, Me)

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Although intensive efforts have been devoted during recent years to prepare and characterize metal-bound CO_2 complexes in conjunction with CO_2 fixation via reactions with transition-metal systems,[2] only a few metal-coordinated CO_2 complexes have been isolated and crystallographically ascertained.[3–6] These include a novel d^6 Ir(III) $IrCl(C_2O_4)(PMe_3)_3$ product[6] in which the C_2O_4 ligand has been formed from a *head-to-tail* O_2C–OCO dimerization of CO_2 by initial reaction with a d^8 Ir(I) complex. On the other hand, the more reactive, related cumulene (or heteroallene) carbon disulfide has been shown from structural studies[2,7,8] to

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(1) (a) Based in part on the Ph.D. thesis of J. J. Maj at the University of Wisconsin—Madison, 1981. (b) On leave from the School of Chemistry, University of New South Wales, Kensington, NSW, 2033, Australia.

(2) (a) Abstracts of International Seminar on the Activation of Carbon Dioxide and Related Heteroallenes on Metal Centers, University of Rennes, Rennes, France, May 20–22, 1981. (b) Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Gaustini, C. *Inorg. Chem.* **1981**, *20*, 349–355 and references therein. (c) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57–73 and references therein.

(3) (a) Aresta, M.; Nobile, C. F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636–637. (b) Aresta, M.; Nobile, C. F. *J. Chem. Soc., Dalton Trans.* **1977**, 708–711.

(4) Fachinetti, G.; Floriani, C.; Zanazzi, P. F. *J. Am. Chem. Soc.* **1978**, *100*, 7405–7407.

(5) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145–1146.

(6) Herskovitz, T.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1976**, 1615–1616.

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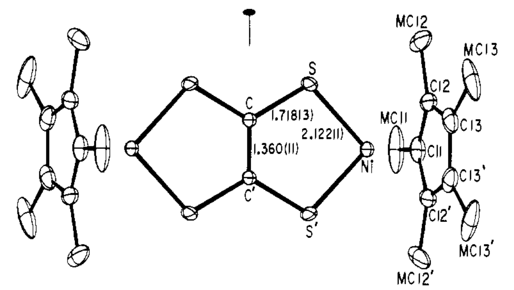

Figure 1. View of the $Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ molecule (**2**), which has crystallographic C_{2h}–$2/m$ site symmetry. The $NiS_2C_2S_2Ni$ core of this bimetallic tetrathiolene complex experimentally possesses a planar D_{2h}–mmm geometry with extensive π-electron delocalization indicated from its bond lengths and redox properties.

display a wide variety of coordination modes in its linkage to one or two metal centers as either a monomer or C–S-coupled dimer. This latter C_2S_4 ligand, which is bound to one rhodium atom in $Rh(\eta^5\text{-}C_5H_5)(PMe_3)(C_2S_4)$ and to two metal–metal-bonded rhodium atoms in $Rh_2(Ph_2PCH_2PPh_2)_2Cl(CO)(C_2S_4)$,[7] is analogous to the previously mentioned iridium-activated C_2O_4 ligand[6] in being similarly formed from a *head-to-tail* S_2C–SCS condensation of a CS_2 molecule with a metal-coordinated CS_2 ligand. Other than a recent communication[9,10] there are no previous reports (to our knowledge) of a metal-activated *head-to-head* dimerization of carbon disulfide to form an ethylenetetrathiolato (or tetrathiooxalato) species[11] containing a C–C bond.

Herein are presented the synthesis and stereochemical characterization of $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_2\text{-}S)]_2(C_2S_4)$ (**1**) and $Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ (**2**), which are of major interest and importance in representing the first metal bis(1,2-dithiolene-like) tetrathiooxalate complexes directly formed from a highly desirable *head-to-head* S_2C–CS_2 dimerization of carbon disulfide through activation on transition-metal centers. The 1,2-dithiolene-type chelation of each of the two $Ni(\eta^5\text{-}C_5Me_5)$ moieties in **2** by the tetradentate C_2S_4 ligand results in the formation of a *planar* $NiS_2C_2S_2Ni$ core containing a highly delocalized π-electron system with reversible redox character as established by cyclic voltammetry. The hexanuclear nickel complex **1** may be considered as an adduct of **2** formed by the net insertion of a $(\eta^5\text{-}C_5H_5)Ni$–S–$Ni(\eta^5\text{-}C_5H_5)$ fragment across each pair of nickel-chelated sulfur atoms in **2** to give two equivalent, six-membered, chairlike $(NiS)_3$ rings.

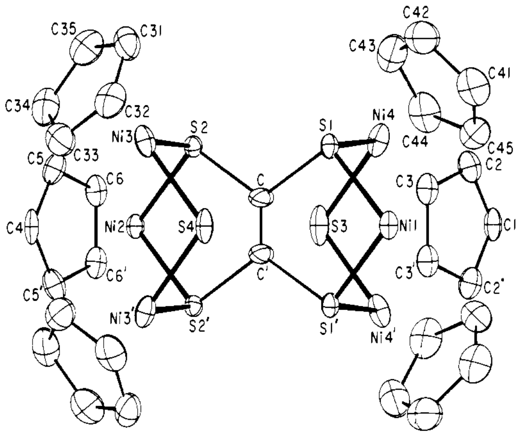

Figure 2. View of the $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}S)]_2(C_2S_4)$ molecule (**1**), which possesses crystallographic C_s–m site symmetry but closely conforms to a C_{2h}–$2/m$ geometry. This hexanickel complex may be viewed as a cycloaddition product of the dinickel molecule **2** (Figure 1) formed by the insertion of a CpNi–S–NiCp fragment across each of the two *cis*-1,2-dithiolato sulfur atoms to give two 2-fold-related, chair-like, six-membered $(NiS)_3$ rings. The fact that the two ethylene carbon atoms possess extremely large out-of-plane thermal ellipsoids indicative of an average structure in which the ethylene carbon atoms occupy at least two orientations in the crystalline state is also reflected in an artificially short C–C′ distance of 1.13 Å which in turn causes the average C–S distance of 1.84 Å to be abnormally long. This presumed ethylene disorder may be attributed to the interaction of the ring sulfur atoms S3 and S4 with C and C′, as indicated from the close S3···C and S4···C distances of 2.27 and 2.28 Å, respectively.

This research arose from our initial efforts to prepare the selenium analogue of the trigonal-bipyramidal Ni_3S_2 cluster $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_3\text{-}S)_2$[12] by the reaction of $Ni_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}CO)_2$ with elemental selenium in carbon disulfide. The unexpected product **1** was subsequently found to be produced without selenium. Our hope from steric considerations that the use of $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$ with its bulky pentamethylcyclopentadienyl ligands in place of unsubstituted cyclopentadienyl ligands would give rise to a simple dinickel tetrathiolene complex was realized with the formation of **2** in essentially quantitative yield.

Reaction of $Ni_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}CO)_2$ with neat CS_2 at 40 °C for several hours produces a black-green solution, from which **1** was obtained as the major product;[13] **2** was isolated as the sole product[14] from the analogous reaction with $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$. Both **1** and **2** have been characterized by spectroscopy[15,16] and X-ray structural determinations.[17-19]

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(7) Werner, H.; Kolb, O.; Feser, R.; Schubert, U. *J. Organomet. Chem.* **1980**, *191*, 283–293 and references therein.

(8) Cowie, M.; Dwight, S. K. *J. Organomet. Chem.* **1981**, *214*, 233–252.

(9) $Fe_4(CO)_{12}(C_2S_4)$ was isolated by Johnson, Lewis, and co-workers[10] in low yield (1–2%) as one of five observed products from the reaction of $Fe_3(CO)_{12}$ with an excess of CS_2 in hexane at 80 °C under a 1:1 CO–Ar mixture. An X-ray crystallographic determination[11] revealed that in this complex two centrosymmetrically related $Fe_2(CO)_6$ units are each attached by both iron atoms to each of two thiolate groups of a C_2S_4 ligand via a 1,1- or 2,2-dithio chelating CS_2 ring linkage (instead of the side-on, 1,2-dithio chelating C_2S_2 ring linkage found in **1** and **2**). The molecular parameters (viz., C–C and C–S bond lengths of 1.33 (1) and 1.77 Å (average), respectively) were viewed[10] in terms of the C_2S_4 ligand being *formally* regarded as a derivative of ethenetetrathiol rather than a tetrathiooxalate ligand. It was stated[10] that this novel compound "also demonstrates the formation of a C–C double bond, a key factor in the synthesis of C_2 or larger organic molecules from single carbon starting materials in homo- or heterogeneously catalyzed reactions".

(10) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1982**, 140–141.

(11) (a) The tetrathiooxalate dianion ($C_2S_4^{2-}$) is an unstable intermediate in the reduction of CS_2 with sodium or potassium in DMF (Steimecke, G.; Sieler, H.-J.; Kirmse, R.; Hoyer, E. *Phosphorus Sulfur* **1979**, *7*, 49–55). (b) An electrochemical preparation from carbon disulfide of tetraalkylammonium salts of the tetrathiooxalate dianion has been recently reported (Jeroschewski, P. *Z. Chem.* **1981**, *21*, 412). (c) The preparation by a multistep organic synthesis of highly conductive poly(metal ethylenetetrathiolate) polymers containing transition metals (including nickel) has been reported (Engler, E. M.; Nichols, K. H.; Patel, V. V.; Rivera, N. M.; Schumaker, R. R., U.S. Appl. 793379, March 31, 1977).

(12) Vahrenkamp, H.; Uchtman, V. A.; Dahl, L. F. *J. Am. Chem. Soc.* **1968**, *90*, 3272–3273.

(13) **1** was isolated by chromatography over alumina (activity III) with toluene solvent.

(14) The CS_2 solution was evaporated and the resulting solid washed with hexane. The product can then be extracted from the insoluble residue with CH_2Cl_2. Estimated yield is >90%.

(15) $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_2\text{-}S)]_2(C_2S_4)$ (**1**): ^1H NMR (C_6D_6 vs. Me_4Si) δ 4.88 (s, C_5H_5, 20 H), 5.08 (s, CH, 10 H). Its diamagnetic character was inferred from the absence of any paramagnetic shift in the ^1H NMR resonances.

(16) $Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ (**2**): ^1H NMR (C_6H_6 vs. Me_4Si) δ 1.56 (s, Me, 30 H); UV–vis λ 1280 (ϵ 22 000), 413 (ϵ 15 000), 375 (ϵ 13 000), 292 nm (ϵ 14 000). A cyclic voltammetric investigation performed on **2** under ambient conditions in CH_2Cl_2 solutions (ca. 10^{-3} M with 0.1 M TBAH as the supporting electrolyte) gave $E_{1/2}$ values (vs. SCE) for the three determined quasi-reversible couples $[Ni_2]^-/[Ni_2]^{2-}$, $[Ni_2]^0/[Ni_2]^-$, and $[Ni_2]^+/[Ni_2]^0$ (where $[Ni_2]$ denotes **2**) of −1.43, −0.92, and +0.09 V, respectively. Magnetic susceptibility measurements via the Faraday method at 20 °C showed **2** to be diamagnetic.

(17) $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu_2\text{-}S)]_2(C_2S_4)\cdot C_6H_6$ (fw 1037.35): parallelepiped-shaped crystals obtained from slow evaporation of a benzene solution; orthorhombic, *Pbcm* (D_{2h}^{11}-no. 57), a = 12.273 (3) Å, b = 17.366 (5) Å, c = 18.077 (9) Å, V = 3853 (2) Å^3, ρ_c = 1.79 g/cm^3 for Z = 4. Our ultimate choice of the centrosymmetric *Pbcm* space group (vs. the corresponding noncentrosymmetric $Pca2_1$ one), which requires crystallographic molecular site symmetry C_s–m for **1**, was based upon the resulting least-squares refinement performed with RAELS.[24] The least-squares refinement converged at $R_1(F)$ = 10.2% and $R_2(F)$ = 10.5% for 1260 independent data [$I > 2\sigma(I)$] obtained via a Syntex (Nicolet) $P\bar{1}$ diffractometer with Mo Kα radiation.

(18) Rae, A. D. "RAELS, A Comprehensive Least-Squares Program"; University of New South Wales, Kensington, 1976; adapted for a Harris/7 computer by A. D. Rae, University of Wisconsin—Madison, 1980.

The dinickel tetrathiolene-like complex **2** (Figure 1) possesses crystallographic C_{2h}–$2/m$ symmetry; the central $NiS_2C_2S_2Ni$ fragment conforms within experimental error to a planar D_{2h} geometry, which is analogous to that of the organic pentalene dianion. Prime evidence that the π system of the bimetallic-coordinated tetrathiooxalate ligand in **2** is highly delocalized (unlike that of the bimetallic-coordinated dithiooxalato ligand[20]) not only is in accordance with its redox behavior[16] but also is consistent with the Ni–S, S–C, and C–C bond lengths of 2.122 (1), 1.718 (3), and 1.360 (11) Å, respectively, being similar to those found[21] in the neutral nickel bis(1,2-dithiolene) complexes. The selective, facile, *head-to-head*, quantitative dimerization of CS_2 in **2** may be attributed to each Ni(I) in the coreactant $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$ functioning as a one-electron reductant as well as a chelating sulfur acceptor. The only previously reported example of a *head-to-head* C–C coupling of another cumulene (or heteroallene) is the reduction of *p*-tolylcarbodiimide by the d^2 Ti(II) $Ti(\eta^5\text{-}C_5H_5)_2(CO)_2$ to the presumed d^1 Ti(III) tetra-*p*-tolyloxalylamidine complex $[(\eta^5\text{-}C_5H_5)_2Ti]_2(C_2(NR)_4)$,[2b] whose planar $Ti(RN)_2C_2(NR)_2Ti$ fragment is strikingly similar to the $NiS_2C_2S_2Ni$ fragment in **2**.

The hexanickel molecule **1** (Figure 2) of crystallographic C_s–m site symmetry closely conforms to a centrosymmetric C_{2h} geometry with the pseudo-2-fold axis directed along the C–C′ bond. Direct evidence for the breakdown of the dithiolene-like electron delocalization due to this formal adduct formation of **1** from **2** is given by the similar values of the six independent Ni–S bond lengths of range 2.160 (6)–2.184 (7) Å and mean 2.173 Å being significantly longer than those in **2**. Formal valence electron considerations suggest that this molecule can likewise be viewed as containing a tetrathiooxalato dianion together with six d^8 Ni(II), six $C_5H_5^-$ ligands, and two S^{2-} ligands.[22–24]

Current studies are underway to determine whether **2** may serve as a convenient chemical precursor to other interesting organic species (e.g., tetrathiofulvalene complexes via reactions with acetylenes). So that the reactivity of $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$ with other cumulenes can be explored, reactions with phenyl isocyanate, diphenylcarbodiimide, various isothiocyanates, COS, and CO_2 are also being carried out.

Acknowledgment. This research was supported by the National Science Foundation. Thanks are due to Mark H. Englert and Mark A. Murphy for their assistance in parts of the experimental work.

Registry No. 1, 82281-75-2; **2**, 82281-72-9; $Ni_2(\eta^5\text{-}C_5H_5)_2(\mu_2\text{-}CO)_2$, 12170-92-2; $Ni_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2$, 69239-93-6; CS_2, 75-15-0.

Supplementary Material Available: Listings of atomic parameters for both $[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}S)]_2(C_2S_4)\cdot C_6H_6$ (Table I) and $Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ (Table II) (4 pages). Ordering information is given on any current masthead page.

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(19) $[Ni_2(\eta^5\text{-}C_5Me_5)_2(C_2S_4)$ (fw 540.16): parallelepiped-shaped crystals acquired from slow evaporation of a benzene solution; the crystal data conform to tetragonal D_{4h} Laue symmetry with $a = b = 12.924$ (6) Å, $c = 14.342$ (5) Å, $V = 2395$ (2) Å^3, $\rho_c = 1.50$ g/cm^3 for $Z = 4$. An incoherent twinning model involving an individual orthorhombic single-crystal component of symmetry *Pbam* was used to solve the crystal structure. The procedures for solving and refining such crystal data which suffer from diffraction enhancement and twinning are given elsewhere.[1a] Least-squares refinement of the twinned structure with RAELS[18] gave $R_1(F) = 4.9\%$ and $R_2(F^2) = 13.8\%$ for 919 independent diffractometry collected reflections with $I > 2.5\sigma(I)$.

(20) Hollander, F. J.; Leitheiser, M.; Coucouvanis, D. *Inorg. Chem.* **1977**, *16*, 1615–1619. Leitheiser, M.; Coucouvanis, D. *Ibid.* **1977**, *16*, 1611–1614 and references cited therein. Coucouvanis, D., In "Transition Metal Chemistry: Current Problems of General, Biological and Catalytic Relevance", Müller, A., Diemann, E.; Eds.; Verlag Chemie GmbH, Weinheim, 1981, pp 59–89.

(21) Eisenberg, R. *Prog. Inorg. Chem.* **1970**, *12*, 295–369.

(22) Alternatively, the bridging C_2S_4 ligand in **1** may be regarded as a tetraanion of ethylenetetrathiol[10,23] coordinated to two electron-coupled d^7 Ni(III) and four d^8 Ni(II). Lappert and co-workers[23,24] have shown that related electron-rich poly(organosulfur) olefins have afforded an extensive metal coordination chemistry via reactions with a variety of transition-metal substrates.

(23) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Pye, P. L. *J. Chem. Soc., Chem. Commun.* **1975**, 683–684.

(24) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Pye, P. L.; Shaw, D. B. *J. Chem. Soc., Dalton Trans.* **1979**, 434–440 and references therein.

Studies of Exciplexes in Mixed Crystals. Activation Energy for a Solid-State Photoaddition Reaction Proceeding via an Exciplex

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Exciplex intermediacy has been postulated for many photoaddition reactions, although the number of such reactions where this species has actually been observed is much smaller.[1] Only in recent years has exciplex intermediacy been demonstrated for certain photoadditions;[2] in most cases this was achieved by showing[2a–f] that certain additives quenched exciplex fluorescence and photoaddition in solution to the same extent without quenching the initial monomer excited state.

In this communication we suggest an alternative approach for studying certain exciplex-forming systems and/or heterophotoaddition reactions, which is based on the use of solid solutions.[3] In this approach the system is studied in a mixed crystal of the interacting species.[4a] The main advantages of the present approach over solution studies are (a) the ground-state geometries of the interacting molecules are fixed and can be determined by various techniques,[5] (b) measurements may usually be performed over a wide temperature range (up to the crystal melting point), which enables determination of activation energies, and (c) energy transfer in crystals is frequently very efficient and so exciplex fluorescence may be observed exclusively, enabling determination of exciplex fluorescence quantum yields and, as shown here, evaluation of the role of an exciplex in a photoaddition reaction.

The above approach is demonstrated by studying the solid-state heterophotodimerization between 9-cyanoanthracene (9-CNA) and 9-methoxyanthracene (9-MeOA) in 9-CNA host crystals doped with 9-MeOA. It has been shown[4a,b] that this system also exhibits exciplex emission. At room temperature a 9-MeOA (guest) concentration of 4% causes quenching of about 95% of the host excited states by exciplex formation;[4a] the major channel of energy transfer through the crystal is the 9-CNA excimer level.[4b,c] At low temperatues (<100 K) when excimer-level transfer is inhibited, the exciplex may nevertheless be populated by direct excitation at tail absorption (450 nm) since the absorption of a mixed crystal containing heteropairs is slightly red-shifted with respect to that of the pure host.[4a]

In the present work it is proven (without the need to introduce supplementary quenchers) that the above-mentioned photodimerization proceeds via the exciplex. Arrhenius-type analysis of exciplex fluorescence parameters yields the activation energy for photodimerization as well as a calculated quantum yield of photodimerization in good agreement with experiment.

Exciplex intermediacy in the photodimerization may be proven or eliminated by simultaneously monitoring the exciplex fluorescence quantum yield (ϕ_F) and decay time (τ) as functions of temperature. It has been observed[4a] that the yield of photoproduct, which is measurable at room temperature, is zero at 77

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(1) For recent reviews see: Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45–50. Lewis, F. D. *Ibid.* **1979**, *12*, 152–158.

(2) (a) Caldwell, R. A.; Smith, L. *J. Am. Chem. Soc.* 1974, *96*, 2994–2996. (b) Creed, D.; Caldwell, R. A. *Ibid.* **1974**, *96*, 7369–7371. (c) Farid, S.; Hartman, S. E.; Doty, J. C.; Williams, J. L. R. *Ibid.* **1975**, *97*, 3697–3702. (d) Lewis, F. D.; Hoyle, C. E. *Ibid.* **1977**, *99*, 3779–3786. (e) Pac, C.; Sakurai, H. *Chem. Lett.* **1976**, 1067–1072. (f) Libman, J.; Ludmer, Z.; Lourie, B.; Yakhot, V. *J. Chem. Res., Synop.* **1978**, 472–473. (g) Ferguson, J.; Mau, A. W.-H. *Mol. Phys.* **1974**, *27*, 377–387.

(3) Kitaigorodsky, A. I. "Molecular Crystals and Molecules"; Academic Press: New York, 1973; pp 94–105.

(4) (a) Berkovic, G. E.; Ludmer, Z. *Chem. Phys.* **1981**, *58*, 57–64. (b) Berkovic, G. E.; Ludmer, Z.; Haas, E. *J. Lumin.* **1981**, *24/25*, 543–546. (c) Ludmer, Z. *Chem. Phys.* **1977**, *26*, 113–121.

(5) The host crystal structure can be accurately determined by X-ray crystallography; the position and conformation of a low concentration of a guest species may be estimated by molecular force-field calculations; see ref 3, pp 115–121. Craig, D. P.; Markey, B. R.; Griewank, A. O. *Chem. Phys. Lett.* **1979**, *62*, 223–229.

0002-7863/82/1504-4280$01.25/0