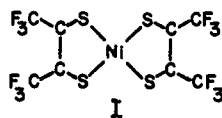# Donor–Acceptor Complexes of the Inorganic π Acceptor, Bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel

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Abstract: Electrically conducting donor–acceptor complexes between the aromatic hydrocarbons perylene and pyrene and the powerful electron acceptor bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel have been prepared. Their crystal structures have been determined from single-crystal X-ray diffraction studies. These 1:1 complexes are found to consist of stacks of alternating organic and inorganic molecules with the stacking axis parallel to the growth axis. The crystals are semiconductors having room-temperature resistivities of the order of 10^5 ohm cm. The activation energy for conduction is anisotropic for the perylene complex with a minimum activation energy along the stacking axis. Absorption bands attributed to an intermolecular charge-transfer transition have maxima in the near-infrared at an energy which is the same as the band-gap energy if the conductivity is assumed to be intrinsic, and if there is no energy barrier for conduction along the stacking axis.

Complexes between electron acceptors and electron donors have been studied extensively.[1] In these complexes, the structure of the individual components remains unchanged but the electrical resistivity of the complex is several orders of magnitude less than that of the isolated components. The absorption spectra of these complexes show new bands where neither of the component molecules absorb, and such bands are attributed to intermolecular charge transfer.[2] Donor–acceptor complexes are described as strong (ionic) or weak (nonionic) depending on the degree of charge transfer in the ground state.[2,3] Both organic molecules and inorganic metal[4] complexes have been used as donors. Acceptors have included organic molecules and simple inorganic molecules such as the halogens.[5] This paper reports the crystal structures and some of the physical properties of donor–acceptor complexes in which the acceptor is the transition metal complex, bis-*cis*-(1,2-perfluoromethylethene-1,2-dithiolato)nickel (nickel thiete) (I),[6] and the donors are the highly conjugated aromatic molecules pyrene and perylene.

I

Experimental Section

Preparation of Complexes. Perylene and pyrene were reagent grade chemicals obtained from the K and K Laboratories. They were purified by recrystallization from benzene and by sublimation, respectively. Nickel thiete was prepared as previously described[6] and recrystallized from pentane. Further purification of these materials for growing crystals to be used for electrical conductivity measurements was done and is described in a later section.

Complexes of both perylene and pyrene with nickel thiete were prepared by mixing benzene solutions containing equimolar amounts of the hydrocarbon and nickel thiete. Large crystals of the perylene complex were grown by allowing a solution of nickel thiete in pentane to diffuse over a period of several days into a solution of perylene in dichloromethane. Large crystals of the pyrene complex could not be grown.

Absorption Spectra. Visible and near-infrared absorption spectra of KBr disk samples were recorded on a Perkin-Elmer Model 621 spectrophotometer. Infrared absorption spectra were recorded on a Perkin-Elmer Model 450 spectrophotometer. To verify that the absorptions were not due to dispersion, blank KBr disks containing only the pure components of the complex were run. No quantitative measurements of absorption intensity were attempted.

Electrical Conductivity and Seebeck Coefficients. The resistance of both single crystals and compressed pellets was measured as a function of temperature. The pellets were pressed with an evacuable KBr die using an applied force of 30,000 lb on a 13-mm piston. A thin layer of silver was pressed on either side of the pellet to ensure good electrical contact.

The resistance of the sample was measured by gluing it to a polystyrene block and attaching thin copper wires to the sample faces using conductive silver paint. The copper wires were soldered to threaded brass rods which were bolted at one end to the polystyrene block and threaded through a Teflon stopper at the other end. The brass rods served as electrical leads to a circuit which consisted of a battery and a shunt resistor in series with the crystal. The voltage drop across the shunt resistor was used to determine the current flow in the circuit from which the resistance of the crystal was calculated. For perylene–nickel thiete the shunt was a precision 10^4-ohm resistor and the voltage drop was measured on the *Y* axis of a Hewlett-Packard XY recorder, Model No. 7001A, which has a 10^6-ohm input impedance. For the pyrene–nickel thiete complex the shunt was a precision 10^8-ohm input resistor to a Cary vibrating reed electrometer, Model 32. The output of the electrometer was measured on the *Y* axis of the same XY

(1) F. Gutman and L. E. Lyons, "Organic Semiconductors," John Wiley & Sons, Inc., New York, N. Y., 1967; J. Kommandeur in "Physics and Chemistry of the Organic Solid State," Vol. 2, D. Fox, M. Labes, and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1965, p 1; and numerous references therein.

(2) R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

(3) H. M. McConnell, B. M. Hoffman, and R. M. Metzger, *Proc. Natl. Acad. Sci. U. S.*, **53**, 46 (1965).

(4) C. K. Prout, R. J. P. Williams, and J. D. Wright, *J. Chem. Soc., A*, 747 (1966).

(5) J. Kommandeur and F. R. Hall, *J. Chem. Phys.*, **34**, 129 (1961).

(6) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963).

recorder used for the perylene–nickel thiete complex. The applied voltages were 45 and 6 V for the perylene and pyrene complexes, respectively. The X axis of the XY recorder was used to measure the output of a copper–constantan thermocouple placed quite near the crystal. In this manner a continuous recording of temperature vs. resistance was obtained.

To vary the temperature, the crystal and polystyrene block were placed in a glass tube closed at the top with the Teflon stopper. The glass tube was placed in a dewar through a styrofoam cover, and cold nitrogen from a liquid nitrogen heat exchanger was passed into the dewar. The temperature inside the dewar could be varied between room temperature and $-100°$. The rate of cooling was controlled by varying the nitrogen flow rate and was kept at about $0.5°/min$. The sample chamber was flushed initially with nitrogen, and a very small flow was maintained during the run. The resistance was measured during cooling and warming and the two values were averaged. The cross-sectional area of the sample was estimated using a Bausch and Lomb X7 magnifier.

For measurements of the Seebeck coefficient, suitable single crystals of perylene–nickel thiete were fixed to two large copper rods using conductive silver paint. A temperature gradient was produced either by cooling one rod with liquid nitrogen or by warming it with boiling water. The voltage developed was measured using the same Cary vibrating reed electrometer as used for conductivity measurements. The temperature differential was determined by fixing two copper–constantan thermocouples to the copper rods. The crystal was kept in an atmosphere of nitrogen during a measurement. In the case of pyrene–nickel thiete the Seebeck coefficient of a compressed pellet was measured. The same procedure was employed as for the perylene–nickel thiete crystals except that the rods were pressed against the pellet by spring tension.

Electron Paramagnetic Resonance Measurements. Epr measurements were made on a Varian V-4502 spectrometer system operating at 9.5 GHz using 100-kHz field modulation. The microwave frequency was measured by means of a Hewlett-Packard Model 2590A frequency converter and Model 5245L frequency counter. The magnetic field was monitored with a proton resonance gauss meter whose frequency was measured by the same frequency counter. Relative spin concentration measurements were made by integrating the first derivative epr signal using a Philbrick integrator, Model UPA-2, and then integrating a second time using a D&E planimeter, Model 62 0015.

Crystallography. Perylene–Nickel Thiete. Precession and Weissenberg photographs indicated that the crystal was triclinic, $a_0 = 12.71 \pm 0.01$ Å, $b_0 = 6.89 \pm 0.01$ Å, $c_0 = 8.41 \pm 0.01$ Å, $\alpha = 87.4 \pm 0.5°$, $\beta = 110.3 \pm 0.5°$, $\gamma = 103.4 \pm 0.5°$. Cu Kα Weissenberg photographs were used to measure a^*, b^*, and γ^*. The other reciprocal cell constants were measured using a precession camera and Mo Kα radiation. The assumption of one donor–acceptor pair per unit cell gave a density calculated from X-ray data of 1.86 g/cc compared with 1.88 g/cc found by flotation methods.

Reflections were collected for $h0l$ on a precession camera using Mo Kα radiation, and from $hk0$ out to $hk6$ on a Nonius integrating Weissenberg camera using Cu Kα radiation; 285 reflections were obtained from the precession camera and 1600 reflections were from the Weissenberg camera. Their intensities were estimated visually by comparison with a set of timed exposures. The data were corrected for Lorentz–polarization as well as absorption ($\mu_r = 1.4$) and the Weissenberg layers were placed on the same relative scale using the $h0l$ intensity data.

All calculations were performed on an IBM 7040 computer with a 32K memory. The Fourier program was a local modification of that developed at the UCLA Crystallographic Laboratories.[7] The Busing-Martin-Levy ORFLS[8] crystallographic least-squares program as modified by Doedens, Dahl, and Blount for rigid groups and Stucky for anomalous dispersion was used in the refinement. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized in the least-squares program.

The atomic scattering powers of Ni(I) and S(0) were corrected for the real and imaginary parts of the anomalous dispersion.[9]

(7) P. Gantzel and H. Hope, unpublished.

(8) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn.

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

Scattering powers for Ni(I), F(−I), S(0), C(0), and H(0) were taken from standard tables.[10] In the last two cycles of least-squares refinement, the data were weighted as follows: $F_o \leq 16.0$, $w = 1.0$; $F_o > 16.0$, $w = 16.0/F_o$.

Pyrene–Nickel Thiete. An oscillation photograph and a zero-layer Weissenberg photograph gave the following cell constants: $c = 7.08 \pm 0.01$ Å, $a^* = 0.0844 \pm 0.0001$ Å^{-1}, $b^* = 0.132 \pm 0.001$ Å^{-1}, and $\gamma^* = 79.4 \pm 0.5°$. Intensity data were collected for the $hk0$ zone only.

Determination of Crystal Structures. Perylene–Nickel Thiete. With only one heavy atom per unit cell the structure was assumed to be centrosymmetric, and an electron density map was calculated based on all signs positive. Images of all the thiete atoms and the perylene carbons were evident. Four cycles of least-squares refinement of the group parameters of the thiete and perylene groups gave a disagreement index (R) of 0.39. Five cycles of least-squares refinement of the isotropic temperature factors and the coordinates of the individual thiete atoms reduced R to 0.20. At this point the nickel, sulfur, and fluorine atoms were allowed to move anisotropically, and the perylene atoms were allowed to move independently. Because of program limitations the thiete and perylene atoms had to be refined separately. Five cycles of least-squares refinement brought R to 0.14. At this point a difference electron density map was calculated and showed probable positions for the six perylene hydrogen atoms. The hydrogen atoms were added as a group, each hydrogen being 1.09 Å from the appropriate carbon. Two more cycles of least-squares refinement gave a final R of 0.134. The maximum positional parameter shift in the last two cycles of refinement was less than one-tenth of the parameter's standard deviation. The final atomic parameters are given in Table I, and

Table I. Final Positional Parameters[a] and Isotropic Temperature Factors[b] for Perylene–Nickel Thiete[c]

Atom	x	y	z	B^b
Ni	0.0	0.0	0.0	d
		Thiete Atoms		
S1	0.1061 (3)	0.2713 (5)	0.1305 (5)	d
S2	0.1455 (3)	−0.0789 (5)	−0.0244 (5)	d
C1	0.243 (1)	0.273 (2)	0.141 (2)	2.3 (2)
C2	0.262 (1)	0.114 (2)	0.071 (2)	2.2 (2)
C3	0.336 (1)	0.449 (2)	0.226 (2)	3.3 (3)
C4	0.376 (1)	0.088 (2)	0.073 (2)	3.2 (3)
F1	0.3027 (9)	0.555 (2)	0.320 (2)	d
F2	0.4333 (7)	0.403 (1)	0.329 (1)	d
F3	0.3679 (9)	0.573 (1)	0.119 (1)	d
F4	0.3652 (7)	−0.044 (1)	−0.041 (1)	d
F5	0.4358 (7)	0.028 (1)	0.222 (1)	d
F6	0.4421 (7)	0.260 (1)	0.044 (1)	d
		Perylene Atoms		
C1	0.068 (1)	0.370 (2)	0.677 (2)	3.5 (3)
C2	0.188 (1)	0.481 (2)	0.734 (2)	3.6 (3)
C3	0.267 (1)	0.408 (2)	0.697 (2)	3.8 (3)
C4	−0.323 (1)	−0.146 (2)	0.414 (2)	3.8 (3)
C5	−0.291 (1)	0.035 (2)	0.500 (2)	3.7 (3)
C6	−0.174 (1)	0.142 (2)	0.560 (2)	3.2 (3)
C7	0.237 (1)	0.223 (2)	0.613 (2)	3.1 (3)
C8	−0.090 (1)	0.076 (2)	0.530 (2)	2.9 (3)
C9	0.119 (1)	0.114 (2)	0.556 (2)	2.5 (2)
C10	0.034 (1)	0.189 (2)	0.590 (2)	2.7 (2)
H1	−0.41	−0.22	0.39	
H2	−0.35	0.10	0.54	
H3	−0.14	0.30	0.64	
H4	0.00	0.43	0.70	
H5	0.21	0.61	0.79	
H6	0.36	0.48	0.73	

[a] Hydrogen atoms were refined as a group. [b] Isotropic temperature factors in Å². [c] Estimated standard deviation of last significant figure appears in parentheses. [d] Treated anisotropically; see Table II.
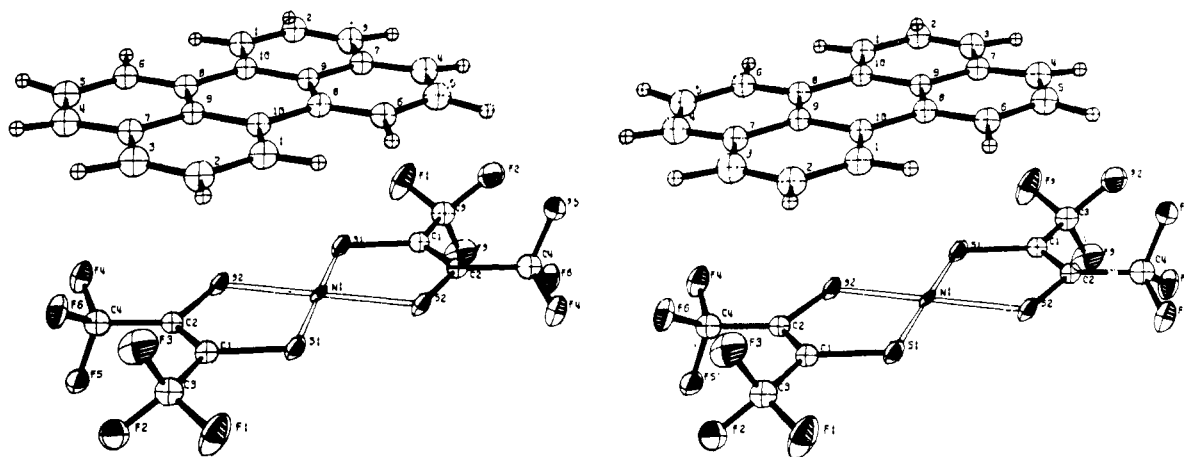
the anisotropic thermal parameters for nickel, sulfur, and fluorine atoms in Table II. The calculated and observed structure factors

(10) J. A. Ibers, ref 9, p 202, Table 3.3.1A.

PERYLENE NICKEL THIETE   PERYLENE NICKEL THIETE

Figure 1. Stereoscopic illustration of one perylene–nickel thiete pair.

have been deposited with NAPS.[11] The final weighted R is 0.17 and the standard deviation of an observation of unit weight is 2.98. An illustration of a perylene–nickel thiete pair is given in Figure 1.

Table II. Anisotropic Temperature Parameters[a] in Perylene–Nickel Thiete

	B_{11}[b,c]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	1.8 (1)	2.6 (1)	1.3 (2)	0.5 (1)	1.3 (1)	0.4 (1)
S1	2.5 (1)	3.1 (1)	2.7 (2)	0.7 (1)	1.6 (1)	−0.4 (1)
S2	2.5 (1)	2.9 (1)	2.7 (2)	0.6 (1)	1.7 (1)	−0.4 (1)
F1	5.3 (5)	5.1 (5)	7.6 (7)	−0.4 (4)	4.3 (5)	−2.9 (5)
F2	3.3 (4)	5.0 (5)	3.6 (5)	−0.2 (3)	1.2 (4)	−0.1 (4)
F3	5.8 (5)	3.6 (4)	5.0 (6)	−0.7 (4)	2.6 (4)	0.7 (4)
F4	3.4 (4)	4.8 (4)	4.9 (6)	1.5 (3)	2.5 (4)	−0.1 (4)
F5	3.0 (4)	6.8 (5)	2.8 (5)	2.2 (4)	1.3 (3)	1.3 (4)
F6	2.7 (4)	4.0 (4)	5.1 (6)	0.5 (3)	2.5 (4)	0.1 (4)

[a] $T_r = \exp[-(h^2 b_{11} + k^2 b_{22} + l^2 b_{33} + 2hk b_{12} + 2hl b_{13} + 2kl b_{23})]$. [b] Listing of $B_{ij} = 4b_{ij}/a^*{}_i a^*{}_j$ where $a^*{}_i$ is the ith reciprocal lattice vector. Units are squared angstroms. [c] Estimated standard deviation of last significant figure appears in parentheses.

Pyrene–Nickel Thiete. A projection of the electron density on the (001) plane was computed assuming all phases positive. The nickel thiete moiety was immediately evident. After several cycles of least-squares refinement of the x, y coordinates of the nickel thiete atoms R was 0.23, and a difference electron density map revealed a crude image of the pyrene molecule. Several cycles of least-squares refinement of the group parameters of the pyrene moiety reduced R to a final value of 0.20.

Results and Discussion

Crystal Structures. The bond lengths and bond angles for the perylene–nickel thiete complex are given in Tables III and IV. Standard deviations were estimated using Cruickshank's method.[12] There is no distortion in the perylene[13] or thiete groups on forming

(11) A table of observed and calculated structure amplitudes of perylene–nickel thiete has been deposited as Document No. NAPS-0298 with the ASIS National Auxiliary Publication Service c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and by remitting $3.00 for photoprints or $1.00 for microfiche. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.
(12) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, 6, 698 (1953).
(13) A. Camerman and J. Trotter, *Proc. Roy. Soc.*, A279, 129 (1964).

a complex as indicated by the small deviations from planarity given in Table V.

Table III. Bond Lengths (Å)[a] in Perylene–Nickel Thiete

Thiete atoms		Perylene atoms[b]	
Bond	Distance	Bond	Distance
Ni–S1	2.124 (3)	C1–C2	1.45 (2)
Ni–S2	2.121 (3)	C2–C3	1.34 (2)
S1–C1	1.70 (1)	C3–C7	1.39 (2)
S2–C2	1.72 (1)	C7–C9	1.44 (2)
C1–C2	1.38 (2)	C9–C10	1.42 (2)
C1–C3	1.48 (2)	C1–C10	1.37 (2)
C2–C4	1.49 (2)	C8–C10	1.50 (2)
C3–F1	1.32 (2)	C6–C8	1.35 (2)
C3–F2	1.34 (2)	C5–C6	1.41 (2)
C3–F3	1.31 (2)	C4–C5	1.37 (2)
C4–F4	1.31 (2)	C4–C7*	1.41 (2)
C4–F5	1.33 (2)	C8–C9*	1.43 (2)
C4–F6	1.35 (2)		

[a] Estimated standard deviation of last significant figure appears in parentheses. [b] * refers to symmetry equivalent atoms.

Table IV. Bond Angles[a] in Perylene–Nickel Thiete

Thiete group[b]		Perylene group[b]	
Angle	Degrees	Angle	Degrees
S1–N S2*	89.6 (1)	C1–C2–C3	120 (1)
S1–N S2	90.4 (1)	C2–C3–C7	121 (1)
Ni–S C1	106.3 (5)	C3–C7–C9	119 (1)
Ni–S2 C2	106.3 (4)	C7–C9–C10	120 (1)
S1–C1–C2	119 (1)	C9–C10–C1	118 (1)
S2–C2–C1	118 (1)	C10–C1–C2	122 (1)
S1–C1–C3	118 (1)	C9–C10–C8	121 (1)
S2–C2–C4	116 (1)	C10–C8–C6	123 (1)
C3–C1–C2	123 (1)	C8–C6–C5	122 (2)
C4–C2–C1	126 (1)	C6–C5–C4	121 (1)
C1–C3–F1	111 (1)	C5–C4–C7*	119 (1)
C1–C3–F2	114 (1)	C3–C7–C4*	120 (1)
C1–C3–F3	113 (1)	C1–C10–C8	122 (1)
C2–C4–F4	112 (1)	C10–C8–C9*	118 (1)
C2–C4–F5	112 (1)	C6–C8–C9*	119 (1)
C2–C4–F6	112 (1)	C4*–C7–C9	121 (1)
F1–C3–F2	106 (1)	C7–C9–C8*	118 (1)
F1–C3–F3	106 (1)	C8*–C9–C10	121 (1)
F2–C3–F3	105 (1)		
F4–C4–F5	107 (1)		
F4–C4–F6	107 (1)		
F5–C4–F6	107 (1)		

[a] Estimated standard deviation of last significant figure appears in parentheses. [b] *refers to symmetry equivalent atoms.

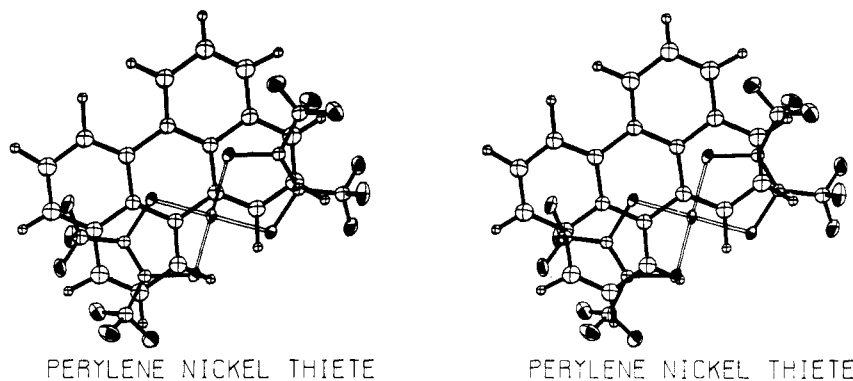PERYLENE NICKEL THIETE   PERYLENE NICKEL THIETE

Figure 2. Stereoscopic illustration of a projection normal to the molecular planes in the perylene–nickel thiete complex.
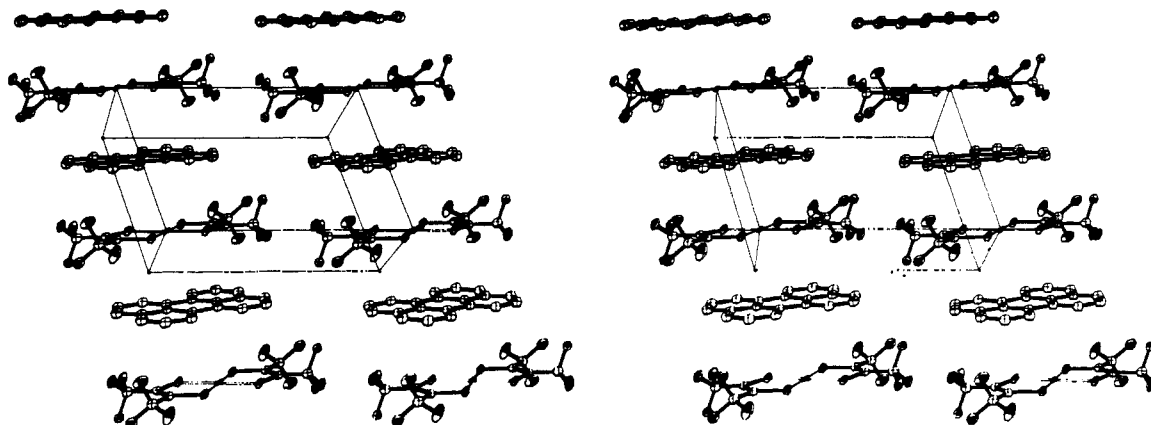

Figure 3. Stereoscopic illustration of the molecular packing of the perylene–nickel thiete complex with a axis horizontal, c axis vertical, and b axis out of page.

Table V. Least-Squares Planes; Perylene–Nickel Thiete

Thiete plane[a]		Perylene plane[b]	
Atom	Distance from plane, Å	Atom	Distance from plane, Å
S1	0.001	C1	0.015
S2	−0.002	C2	0.013
C1	−0.003	C3	−0.034
C2	−0.008	C4	−0.023
C3	−0.015	C5	−0.019
C4	0.032	C6	0.015
		C7	−0.010
		C8	−0.009
		C9	−0.018
		C10	0.007

[a] Thiete plane: $-0.15601X - 0.46656Y + 0.87062Z = 0.0000$.
[b] Perylene plane: $-0.14049X - 0.47606Y + 0.86812Z = 3.5383$.

The molecular packing of the perylene–nickel thiete complex is illustrated in Figures 2–4. Figure 2 illustrates the overlap between the perylene and the nickel thiete molecules. This unsymmetrical overlap probably is due to crystal-packing forces which cause a tilting of the molecular planes with respect to the c axis, the stacking axis, of 32°.

The two-dimensional X-ray data for the pyrene–nickel thiete complex indicate a more symmetrical overlap. The best fit for the $hk0$ projection was obtained with the pyrene situated directly above the nickel thiete. Assuming the molecular planes of the pyrene and nickel thiete molecules are parallel, the maximum interplanar spacing is half the c axis or 3.54

Å. This is the same as the average interplanar spacing in the perylene–nickel thiete complex. An interplanar spacing much less than 3.54 Å would result in strong van der Waals repulsions between the fluorines and the pyrene carbon atoms. Assuming a minimum interplanar spacing of 3.4 Å, the maximum tilt of the molecular planes with respect to the c axis would be 11°.

Electronic Structure. One question which arises about the nature of a donor–acceptor complex is whether the ground state is ionic or neutral,[3] that is, whether the complex is composed of neutral perylene and nickel thiete molecules or of perylene positive ions and nickel thiete negative ions. In reduction of neutral nickel thiete to the negative ion, an electron enters a b_{3g} molecular orbital which is extensively delocalized over the ligands.[14] The b_{3g} orbital is an antibonding metal–ligand orbital, and consequently one expects the nickel–sulfur bond length to increase on reduction of the neutral molecule to the anion. The nickel–sulfur bond length in the perylene–nickel thiete complex, 2.122 ± 0.003 Å, is significantly shorter than the nickel–sulfur bond length in $(C_7H_7)^+(NiS_4C_4(CF_3)_4)^-$,[15] 2.135 ± 0.003 Å. The only other neutral square-planar nickel

(14) R. D. Schmitt and A. H. Maki, *J. Amer. Chem. Soc.*, **90**, 2288 (1968).

(15) R. M. W. and R. L. Schlupp, submitted for publication. The classification of $NiS_4C_4(CF_3)_4$ molecule as a monoanion in the tropylium complex is based on the g tensor obtained from a magnetically concentrated powder epr spectrum, in which the known g values of NiS_4C_4-$(CF_3)_4^-$ [6] have been averaged by electron spin exchange between the two magnetically inequivalent molecules in the unit cell.
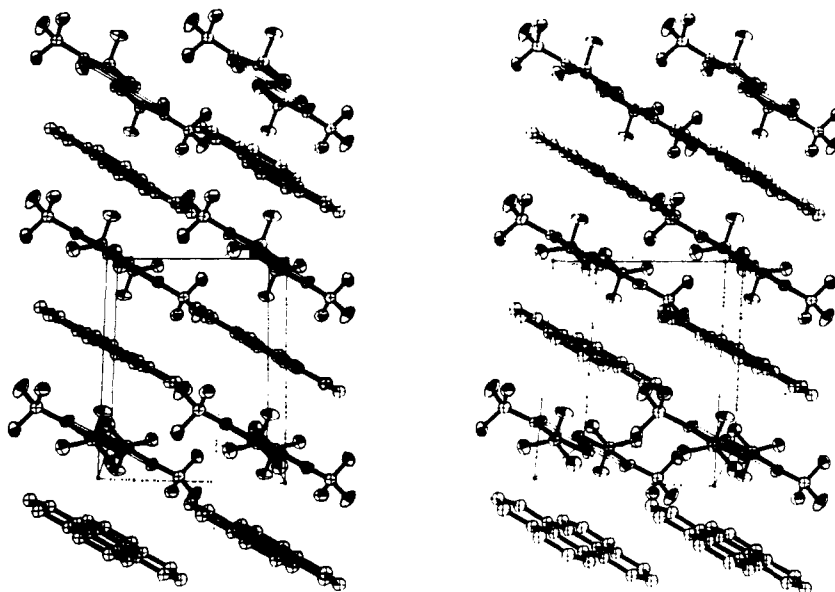
Figure 4. Stereoscopic illustration of the molecular packing of the perylene-nickel thiete complex with b axis horizontal, c axis vertical, and a axis out of page.
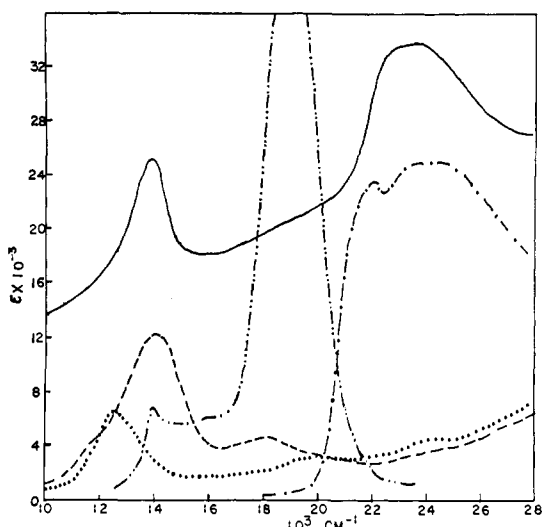

Figure 5. Optical absorption spectra of (——) $NiS_4C_4(CF_3)_4$, (····) $[(C_2H_5)_4N][NiS_4C_4(CF_3)_4]$, (–·–·) perylene, (–··–··) perylene positive ion, and (——) perylene-nickel thiete complex. All spectra were recorded using the KBr disk method. Molar extinction coefficients were taken from references given in the text for all compounds except the perylene-nickel thiete complex which is on an arbitrary scale.

bisdithiolene complex in which the nickel-sulfur bond length has been measured is the structurally similar $NiS_4C_4(C_6H_5)_4$ complex.[16] Here the nickel-sulfur bond length is 2.101 ± 0.002 Å, which is shorter than the nickel-sulfur bond length in the perylene-nickel thiete complex, but we feel that comparisons should not be made between square-planar complexes with very dissimilar R groups. The strongly electron-withdrawing perfluoromethyl groups are expected to reduce the bond order in the five-membered chelate ring, and this would be expected to lead to a longer nickel-sulfur bond in nickel thiete.

Another indication of the ionic or covalent character of the ground state of a donor-acceptor complex is

obtained from the optical absorption spectra. The visible spectra of neutral and anionic nickel thiete, and neutral and cationic perylene, are shown in Figure 5, along with the spectrum of the perylene-nickel thiete complex. There are two characteristic peaks in the visible absorption spectra of neutral nickel thiete and its monoanion. An absorption at 14,000 cm^{-1} (ϵ 12,400)[6] in neutral nickel thiete shifts to 12,400 cm^{-1} (ϵ 6480)[6] in the monoanion; and two absorptions at 20,000 cm^{-1} (ϵ 3800) and 24,000 cm^{-1} (ϵ 5600) are absent in the neutral molecule. The low-energy band occurs at 14,000 and 14,500 cm^{-1} in the perylene and pyrene complexes, respectively, and the bands centered around 22,000 cm^{-1} in the monoanion are absent in both complexes. An absorption at 23,000 cm^{-1} in the perylene-nickel thiete complex can be assigned to the absorption that occurs at 23,000 cm^{-1} (ϵ 25,000) in neutral perylene.[17] Strong absorptions at 19,000 cm^{-1} (ϵ 53,000) and 15,000 cm^{-1} (ϵ 11,000)[18] found in the absorption spectra of the perylene positive ion but not in neutral perylene are absent in the donor-acceptor complex. Similarly, strong absorptions at 20,000 cm^{-1} (ϵ 10,000) and 13,000 cm^{-1} (ϵ 6500)[18] in the spectrum of the pyrene positive ion do not occur in the pyrene-nickel thiete spectrum. The absorption spectra of the aromatic complexes with nickel thiete are thus a superposition of the spectra of the neutral aromatics and nickel thiete and not of the aromatic positive ion and the nickel thiete negative ion, and an upper limit of 5% can be placed on the population of the ionic state at room temperature.

As with most donor-acceptor complexes an absorption band which does not occur in either isolated component molecule occurs in the complex.[2] This band is usually called the charge-transfer absorption. The energies of the maxima in the charge-transfer absorption for the pyrene and perylene complexes are given in

(16) D. Sartain and M. R. Truter, *J. Chem. Soc., A*, 1264 (1967).

(17) G. J. Hoijtink, N. H. Velthorst, and P. J. Zandstra, *Mol. Phys.*, 3, 533 (1960).
(18) W. Ij. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.*, 3049 (1959).

Table VI. This absorption is thought to be due to a transition from the ground-state singlet of the donor–acceptor pair to the first excited singlet.[2,3]

Table VI. Conductivity Parameters and Charge-Transfer Bands

	Direction	ϵ, eV^a	ρ_∞,[a] ohm cm	2ϵ, cm^{-1}	E, cm^{-1} [b]
Perylene	c	0.23	0.05	3800	
	c × a*	0.32	0.06	5200	4000[c]
	a*	0.41	0.008	6700	
	Polycrystalline	0.37	0.09	6100	
Pyrene	c	0.54	0.00006	8700	8500[d]
	Polycrystalline	0.32	512	5100	

[a] From the equation $\rho = \rho_\infty e^{\epsilon/kT}$ using data from dark conductance. [b] Energy of charge-transfer absorption at maximum. [c] Width at half-intensity is 3000 cm^{-1}. [d] Poorly resolved doublet with a total width at half-intensity of 2300 cm^{-1}.

Although a weak epr signal was detected for both the perylene and pyrene complexes, this paramagnetism is probably due to an impurity, with the bulk of the complexes being diamagnetic. If the ground state of the crystal were ionic, we would expect the complexes to be quite paramagnetic at room temperature since both the perylene positive ion and the nickel thiete negative ion are paramagnetic. Generally, ionic donor–acceptor complexes in which the isolated ions are paramagnetic have been found to give strong epr signals.[19,20] Although a spin-pairing mechanism such as occurs in the $[(C_2H_5)_4N]NiS_4C_4(CN)_4$ crystal[21] could result in a diamagnetic ionic ground state, a diamagnetic complex is consistent with a neutral ground state.

The weak signals observed are not expected to be due to the charge-transfer triplet state since it is too high in energy to be significantly populated at attainable temperatures. The epr spectrum of polycrystalline powders of both complexes showed a rhombic g tensor with principal values equivalent to those of the nickel thiete monoanion.[6] Single-crystal epr spectra of the perylene–nickel thiete complex showed that the g tensor had the principal values of the nickel thiete monoanion[6] and the principal directions of the nickel thiete moiety in the crystal. Also, the epr intensity obeyed Curie's law within experimental error. These results indicate that the paramagnetism is due to electrons occurring on nickel thiete molecules in their regular lattice sites, and not from an excited state associated with the electrical conduction. No epr due to paramagnetic cations was detected, either as a separate signal or as a contributor by exchange to the principal tensor values of the observed signal.

Electrical Properties. Both the perylene and pyrene complexes with nickel thiete were found to be moderately good electrical conductors. Plots of the logarithm of the resistivity vs. reciprocal temperature for the perylene complex are given in Figure 6. The resistivity of a single crystal of the perylene complex was measured

(19) P. L. Nordio, Z. G. Soos, and H. M. McConnell, *Ann. Rev. Phys Chem.*, 17, 237 (1966).
(20) R. D. Schmitt, R. L. Schlupp, and A. H. Maki, unpublished results, have found that complexes of nickel thiete with better electron donors, such as aromatic diamines, invariably give strong epr signals.
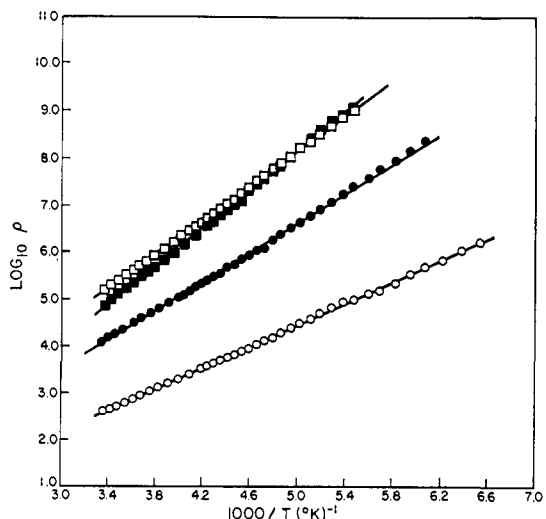(21) J. F. Weiher, L. R. Melby, and R. E. Benson, *J. Amer. Chem. Soc.*, 86, 4329 (1964).

Figure 6. Log of resistivity vs. reciprocal temperature for the perylene–nickel thiete complex: □, compressed powder; O, ●, and ■ refer to resistivity of a single crystal with the current flow in the c, c × a*, and a* directions, respectively.

in three directions and as a compressed pellet. Crystals of the pyrene complex large enough to measure the resistivity in any direction but the growth axis could not be grown. As with most donor–acceptor complexes, the resistivity follows the equation $\rho = \rho_\infty e^{\epsilon/kT}$, where ρ is the resistivity, ϵ an activation energy, k the Boltzmann constant, and T the temperature in degrees Kelvin. The activation energies and intercepts obtained using this equation are given in Table VI, for both the single-crystal and compressed-pellet measurements.

Two samples of the perylene–nickel thiete crystals were studied. The first crystals were grown using reagent grade perylene and once-recrystallized nickel thiete. A second crop of crystals was grown using perylene which had been chromatographed and sublimed, and using nickel thiete which had been three times recrystallized and sublimed. Solvents used for growing the latter crystals were distilled from phosphorus pentoxide and degassed on a high-vacuum system using the freeze-thaw technique. The sublimers and solvents were opened under a nitrogen atomosphere, and the crystals were grown in a nitrogen atmosphere. Both crops of crystals gave the same conductivity plots, indicating that impurities probably do not play a major role in the conduction mechanism. A high concentration of charge carriers also indicates that the conductivity is intrinsic. Assuming an upper limit to the mobility equal to that of an electron in a metal (10 cm^2/V sec) and using the extrapolated value of the conductivity at infinite temperature, a lower limit on the density of states can be calculated from the conductance equation $\sigma_\infty = zen\mu$ where σ_∞ = limiting conductivity, ze = charge of the conducting particle, n = density of states, and μ = mobility. The lower limits thus calculated are $n = 10^{19}$ and 10^{21} cm^{-3} for the perylene and pyrene complexes, respectively. Comparing this to the number of molecules/cm^3 in the complexes (3 × 10^{20}) indicates that the conductivity is intrinsic, since such a high concentration of impurities is unlikely.

The activation energy associated with the generation of charge carriers is not expected to be anisotropic. Any anisotropy is generally due to the variation of the mobility with the different directions of conduction. However, once a charge is generated in the conduction band, there may still be a potential barrier which must be overcome before the charge can be transported to the next molecule. If such a potential barrier existed, the measured ϵ would be the sum of the conduction band-gap plus this potential barrier. The potential barrier for propagation of charge could depend on the direction of propagation and would thus explain the variation in the measured activation energy with direction. The activation energy for the perylene–nickel thiete complex was found to depend on the direction of conduction, with a minimum energy along the direction of greatest overlap of the π orbitals of the perylene and nickel thiete molecules. The data would suggest that there is a large potential barrier to propagation of charge along a direction of small π-orbital overlap. For polycrystalline samples, the conductivity is apparently limited by the directions of highest resistance[22] as is predicted if one averages the resistance over all directions in a single crystal. Thus for perylene–nickel thiete the conductivity of the polycrystalline pellet was similar to the conductivity of the single crystal in the a^* direction, the direction of highest resistance. Since we could not grow crystals of pyrene–nickel thiete large enough to measure the conductivity in any direction but the growth axis, the conductivity of a polycrystalline sample should give us a measure of any anisotropy in the conduction. Since the π-orbital overlap in the pyrene–nickel thiete complex is directed nearly along the stacking axis, a more anisotropic conductivity is expected if the π-orbital overlap provides the mechanism for charge transport. The resistivity of the compressed pellet of pyrene–nickel thiete was much higher than the resistivity along the stacking axis of the crystal but the activation energy was lower. An activation energy for the polycrystalline sample which is lower than the activation energy for the single crystal indicates that the resistance in the polycrystalline sample is dominated by a different conduction process. This may be due to a contact resistance or to a high resistance at grain boundaries in the compressed pellet.

For a donor–acceptor complex with a covalent ground state the first excited state is a state resulting in the transfer of an electron from the donor to the lowest vacant orbital of the acceptor, and can be either a singlet or a triplet depending on whether the spins are parallel or antiparallel. The triplet state is lower in energy than the singlet state, but since optical singlet–triplet transitions are forbidden, the triplet energy cannot be measured by optical absorption. Both the singlet and triplet states can propagate through the crystal as excitons but cannot contribute to electrical conduction since the charges are coulomb bound. To contribute to conduction the charges must be separated so that they may move independently. The state corresponding to positive holes moving on the donor molecules and electrons moving on acceptor molecules should be a conduction state,[3] and be above the lowest excited ionic state energy by an amount equal to the energy necessary to separate the charges, minus any polarization energy gained by having separated charges rather than coulomb-bound charges in the lattice. If we assume that the measured minimum activation energy for conduction represents the conduction band gap, the first excited singlet (charge-transfer) state is quite close in energy to the conduction state for both the pyrene and perylene complexes. However, the ionic triplet state is lower in energy than the singlet state, suggesting that the singlet–triplet splitting in the excited ionic state is approximately the same as the coulomb energy of a coupled electron–hole pair minus the polarization energy. Since the singlet–triplet splitting in the ionic excited state is expected to be small,[3] the coulomb energy consequently must be nearly equal to the polarization energy. The polarization energy of a single charge in perylene and pyrene has been estimated to be 1.9 and 1.7 eV, respectively.[23] The polarization energy of a charge in nickel thiete would be somewhat greater than the polarization energy in perylene because of the heavier, more polarizable atoms, but the total polarization energy from both holes and electrons in the donor–acceptor complexes should be on the order of twice the polarization energy of perylene, 3.8 eV. The attractive ion–ion coulomb energy for linear donor–acceptor complexes with a 3.5-Å separation has been estimated to be 2 to 3 eV.[3] Thus the polarization energy and the coulomb energy appear to be of the same order of magnitude and may cancel.

The Seebeck coefficients, $Q = \Delta V/\Delta T$ were -1.4 mV/deg for a single crystal of the perylene–nickel thiete complex and -1.0 mV/deg for a compressed pellet of the pyrene–nickel thiete complex, indicating that the majority carriers are electrons in both cases. The Seebeck coefficient was constant within experimental error from -10 to $+30°$ for the perylene complex and from -30 to $+20°$ for the pyrene–nickel thiete complex.

Summary and Conclusions

Nickel thiete has been shown to form stable 1:1 complexes with perylene and pyrene. The complexes can be characterized as weak or covalent in that the extent of transfer of an electron from the aromatic to nickel thiete is small in the ground state. The electrical conductivity has been shown to depend on the direction in the crystal and is a maximum in the direction of greatest π-orbital overlap. This variation of the conductivity with direction is found to be due to a variation in the activation energy for conduction, perhaps indicating that there is a potential barrier to the propagation of charge which is maximum in a direction of small π-orbital overlap. The complexes appear to be intrinsic semiconductors. The conduction state is quite close in energy to the first excited singlet (charge-transfer) state as determined from the maximum in the charge-transfer absorption band, although the first excited singlet (or triplet) state is not expected to be a conduction state. This observation leads to the conclusion that the coulomb energy binding the charge pair in these systems is approximately equal to the gain

(22) P. L. Kronick and M. M. Labes, *J. Chem. Phys.*, 35, 2016 (1961).

(23) Reference 1, p 345.

in polarization energy in forming charge carriers. The majority carriers are electrons. Weak epr signals whose intensity follows Curie's law can be attributed entirely to impurity nickel thiete monoanions in the lattice.

Complexation Kinetics of Sarcosine with Nickel(II), Cobalt(II), and Copper(II)[1]

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Abstract: The kinetics of sarcosine complexation with nickel(II), cobalt(II), and copper(II) have been determined by temperature jump. The reactions were of the type $ML_{n-1} + L \rightleftharpoons ML_n (k_n, k_{-n})$, where $M = Ni^{2+}, Co^{2+}$, or Cu^{2+}, L refers to the anionic form of the ligand, and $n = 1, 2$, or 3. At ionic strength 0.1 M and 25° the rate constants are: Ni^{2+}, $k_1 = 1.3 \times 10^4 M^{-1} sec^{-1}$, $k_{-1} = 4.1 \times 10^{-2} sec^{-1}$, $k_2 = 1.2 \times 10^4 M^{-1} sec^{-1}$, $k_{-2} = 0.50 sec^{-1}$, $k_3 \sim 5 \times 10^3 M^{-1} sec^{-1}$, $k_{-3} \sim 5 sec^{-1}$; Co^{2+}, $k_1 = 9.2 \times 10^5 M^{-1} sec^{-1}$, $k_{-1} = 57 sec^{-1}$, $k_2 = 1.5 \times 10^6 M^{-1} sec^{-1}$, $k_{-2} = 5.7 \times 10^2 sec^{-1}$; Cu^{2+}, $k_1 = 2.8 \times 10^9 M^{-1} sec^{-1}$, $k_{-1} = 32 sec^{-1}$, $k_2 = 1.0 \times 10^8 M^{-1} sec^{-1}$, $k_{-2} = 22 sec^{-1}$. The cobalt kinetics follow the dissociative mechanism for sarcosine. However, in the nickel complexation kinetics, formation of the mono and bis complexes appears to be relatively slow, indicating that the N-bonded methyl group in sarcosine has an influential role. As observed with cobalt, formation of the copper–sarcosinate complex is normal. Unlike cobalt, the formation of the bis complex is relatively slow.

The studies of nickel(II) and cobalt(II) with glycine,[3] the oligoglycines,[3] and glycylsarcosine[4] yielded several interesting results. First, for each of the metal ions, the same rate constant was obtained for the formation of the monosubstituted complexes ML, for L = glycylglycinate−, glycylglycylglycinate−, tetraglycinate−, or glycylsarcosinate−. (The values are $\sim 3 \times 10^5 M^{-1} sec^{-1}$ for cobalt(II) and $\sim 2 \times 10^3 M^{-1} sec^{-1}$ for nickel(II).) However, these values are appreciably smaller than the rate constants for the formation of the ML complex of glycine. The effect is more significant for nickel than for cobalt, the ratio of rate constants being 20 in the former case and 5 in the latter.

The rate constants for the formation of the bis species indicated further differences in the behavior of the two metal ions. For nickel(II), the observed rate constants were the same for all four peptides, and the ratio of the rate constants for the two complex formation steps (k_2/k_1) is greater than unity, actually about four. However, for cobalt(II), the observed rate constant, k_2, for glycylsarcosine is four times greater than that for the oligoglycines, with the rate constants for the oligoglycines in good agreement. Furthermore, the ratio of the rate constants, k_2/k_1, is slightly less than 1 for cobalt(II) with the oligoglycines. These results led us to conclude that the bonding model for cobalt–oligopeptide complexes is quite likely different from that for the nickel–oligopeptides.

To determine whether the presence of a methyl group at a binding site could account for the kinetic differences noted for the reactions of nickel(II) and cobalt(II) with glycylsarcosine, we have studied the complexation kinetics of these metal ions with sarcosine (N-methylglycine). We have also examined the copper(II)–sarcosine system, the results of which prove useful in interpreting the kinetics for the other two metal ions.

Experimental Section

The temperature-jump apparatus used for the present experiments was constructed by the Enfield Specialty Co. The temperature jump of nearly 10° was caused by discharging a 0.1-μF capacitor, charged to approximately 25 kV, through the solution. The rise time of the instrument was measured as 15 μsec at an ionic strength of 0.1 M using phenol red as indicator.

The light source is a Hanovia Division mercury–xenon arc lamp. The light passes through an interference filter, through the temperature-jump cell, and impinges upon a Dumont KM 2433 photomultiplier. The change in absorbancy which occurs as the equilibrium is shifted after the temperature jump is recorded on a storage oscilloscope and subsequently photographed.

The sarcosine used in these studies was obtained from Nutritional Biochemicals Corp. Baker reagent grade nitrate salts of potassium, cobalt, nickel, and copper were used. Stock solutions of the transition metal ions were prepared, and the concentrations of these solutions were determined using standard analytic techniques.

The indicators used in this study were Allied Chemical methyl orange, methyl red, chlorophenol red, and phenol red and Eastman Organic bromothymol blue.

Solutions were freshly prepared from solid sarcosine and stock solutions of KNO_3 and the appropriate metal ion and indicator. The solutions were degassed and the pH was adjusted by the dropwise addition of dilute NaOH and/or HNO_3 to ±0.01 pH unit.

Each relaxation time represents an average of at least three photographic determinations. The relative error for these measurements is ±10%. Test solutions of either metal ion or ligand in the absence of the other showed no discernible relaxation effects. These "blank" experiments were carried out at concentration levels of the free metal ion and ligand characteristic of solutions containing

(1) The authors gratefully acknowledge partial support from the Petroleum Research Fund for Grant 2982B and to the Public Health Service for Research Grant GM-08893-07 from the National Institute of General Medical Sciences, Public Health Service, to K. K.

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