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Crystal and Molecular Structures of Ion Radical Molecular Complexes of *cis*-Bis(trifluoromethylethylene-1,2-dithiolato)nickel with Phenothiazine and Phenoxazine. Effects of Donor–Acceptor Separation on the Molecular Properties

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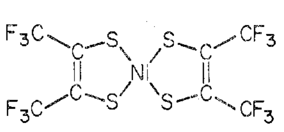
cis-Bis(trifluoromethylethylene-1,2-dithiolato)nickel, Ni(tfd)$_2$, was previously shown to form 1:1 molecular complexes with either phenothiazine (PTZ) or phenoxazine (POZ) in which the ground state is composed of a pair of ion radicals, *e.g.*, PTZ^+–$Ni(tfd)_2^-$. The crystal and molecular structures of both complexes have been determined using the normal ϕ-scan method with Ni-filtered Cu Kα radiation. A total of 2246 and 1351 intensities were collected for PTZ–Ni(tfd)$_2$ and POZ–Ni(tfd)$_2$, respectively. Full-matrix least-squares refinement led to a final R index of 0.065 for PTZ–Ni(tfd)$_2$ and 0.050 for POZ–Ni(tfd)$_2$. Both complexes yield triclinic crystals of space group $P\bar{1}$. PTZ–Ni(tfd)$_2$ has cell dimensions a = 8.886 (7) Å, b = 11.733 (9) Å, c = 12.00 (1) Å, α = 88.1 (5)°, β = 76.6 (5)°, γ = 83.4 (5)°, and Z = 2, and the equivalent dimensions for POZ–Ni(tfd)$_2$ are a = 7.041 (6) Å, b = 7.612 (6) Å, c = 12.57 (1) Å, α = 104.8 (5)°, β = 101.5 (5)°, γ = 103.3 (5)°, and Z = 1. PTZ–Ni(tfd)$_2$ has a ...DDAA... stacking sequence (D = PTZ), the first reported instance of such a sequence in a 1:1 molecular complex. The D–A distance of 3.36 Å is within the normal range for strong donor–acceptor interactions, but the D–D and A–A distances are too great to allow the D–A interactions to be transmitted through the entire stack. POZ–Ni(tfd)$_2$ stacks in the ...DADA... fashion normally encountered in 1:1 π molecular complexes, but the D–A distance of 3.66 Å is too large to allow strong coupling between donor and acceptor molecules. The previously reported physical properties of the complexes are discussed in terms of the structural data. Finally, the phenothiazine cation radical is shown to be nonplanar, whereas the phenoxazine cation radical is planar.

Introduction

In recent years, increasing attention has been paid to donor–acceptor molecular complexes composed of ion pairs, which sometimes exhibit an electronic absorption charge-transfer (CT) band due to excitation from an ionic ground state to a less ionic excited state ($D^+A^- \rightarrow DA$).[2-14] This transition has been called a "reverse charge transfer" because most molecular charge-transfer complexes have neutral ground states and exhibit a $DA \rightarrow D^+A^-$ transition.[15] In almost all cases involving ion-pair ground-state complexes, at least one ion has been diamagnetic,[16] and only two systems appear to have been studied in which both ions are radicals.[6,7] One of these involves the classically important *N,N,N',N'*-tetramethylphenylenediaminetetrachloro-*p*-benzoquinone complex ($TMPD^+$–TCQ^- ground state), for which Anex and Hill observed the reverse charge-transfer band in the reflectance spectrum of a single crystal of the complex.[6a] The other contribution in this area[7] concerned 1:1 complexes of *cis*-bis(trifluoromethylethylene-1,2-dithiolato)nickel, Ni(tfd)$_2$ (**1**), with either phenothiazine, PTZ (**2a**), or phenoxazine, POZ (**2b**). Each of these latter complexes was shown by optical spectroscopy to contain a ground state composed of paramagnetic metal complex anions and phenothiazine or phenoxazine radical cations (*e.g.*, PTZ^+–$Ni(tfd)_2^-$). In spite of the similarity in structure and oxidation potentials[7] of the two different donor molecules,[17] remarkably different solid-state properties were observed for the two complexes. PTZ–Ni(tfd)$_2$ demonstrated strong interactions between the donor and acceptor radical ions in its magnetic susceptibility behavior (consistent with a spin-pairing ground-state singlet and a thermodynamically populated triplet) and optical absorption spectrum (intense "reverse" CT band at 7.8 kK). In marked contrast, POZ–Ni(tfd)$_2$ showed Curie–Weiss magnetic behavior (two independent spins per D^+A^- pair) and no clearly assignable CT interaction,[18] indicating relative independence of the donor and acceptor π systems. Each complex, when dissolved in dichloromethane, showed evidence for ion pairing at low temperatures, but only the phenothiazine complex indicated formation of *tight* ion pairs (*via* observation of the 7.8-kK charge-transfer band in the optical spectrum and observation of abnormal line shapes in its solution esr spectra).



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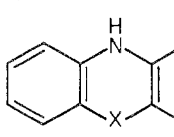

2a, X = S
b, X = O

The X-ray structure determination of these complexes was undertaken in the expectation that knowledge of the crystal structures of the two complexes would lead to a better understanding of the forces important in determining the behavior of these radical–radical ion pairs observed both in the solid and in solution. An additional objective was to ascertain the structure of the phenothiazine cation. Neutral phenothiazine is folded along the N···S axis,[19] and the cation radical has been assumed to be nonplanar,[13,20] but no previous experimental verification of its structure had been reported.

Experimental Section

PTZ–Ni(tfd)$_2$ crystals suitable for X-ray analysis were formed by mixing hot benzene solutions containing equimolar amounts of Ni(tfd)$_2$ and phenothiazine. The resulting crystals were washed with pentane. POZ–Ni(tfd)$_2$ was recrystallized from benzene.[7]

PTZ–Ni(tfd)$_2$. The crystals were dark brown and tabular with a tendency toward elongation in what was later defined as the c-axial direction. Unit cell dimensions, from carefully measured precession photographs (utilizing Zr-filtered Mo Kα radiation at room temperature) yielded a = 8.866 (7) Å, b = 11.733 (9) Å, c = 12.00 (1) Å, α = 88.1 (5)°, β = 76.6 (5)°, γ = 83.4 (5)°, and Z = 2. Precession photographs exhibited no systematic extinctions and thus the space group was determined as $P\bar{1}$ or $P1$.

The observed density, using the sink–float method, was found to be 1.97 g/cm^3, in good agreement with the calculated density of 1.96 g/cm^3 based on Z = 2.

A singly terminated crystal fragment of PTZ–Ni(tfd)$_2$ with dimensions 0.21 × 0.04 × 0.34 mm was selected for data collection, utilizing a computer-controlled, superequiinclination two-circle goniometer with scintillation counter and Ni-filtered Cu Kα radiation. Scan speed was allowed to vary from 1 to 5°/min with the actual value calculated on line as a function of the size of the peak being scanned, thereby tending to balance the counting statistics for all reflections. A rapid preliminary scan was used for the purpose of calculating the optimal scan speed. Background counts were taken for half the scan time and the counter angle (υ) was limited to a

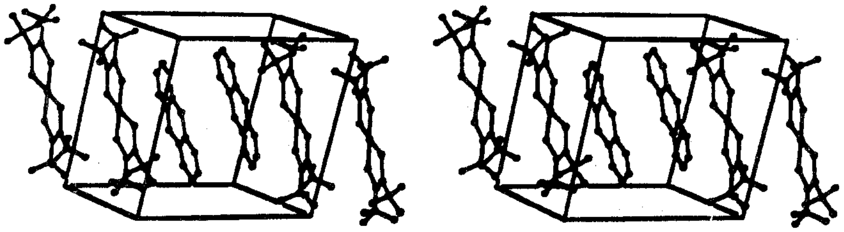

Figure 1. Stereoscopic illustration showing the donor–acceptor sequence in the PTZ–Ni(tfd)$_2$ complex. (The origin is at the lower left back corner with +*a* emerging from the paper, +*b* horizontal, and +*c* vertical.)

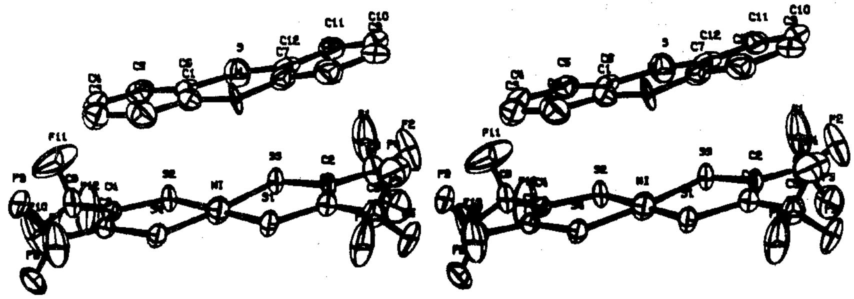

Figure 2. Stereoscopic illustration of one donor–acceptor pair in the PTZ–Ni(tfd)$_2$ complex.

maximum of 90°. Standard reflections, rechecked periodically, indicated no system instability during the 3 weeks of data acquisition. After collection of 2246 reflections, data collection was complete.

The X-ray intensities were then corrected for *Lp* and absorption (μ = 60.8 cm^{-1}) effects utilizing the ACAC program of Prewitt.[21] This and all subsequent computer calculations were performed on an IBM 370/155.

POZ–Ni(tfd)$_2$. All crystals were black to dark brown and extremely platey with a tendency toward elongation in the *b* direction. Precession photographs yielded the following cell parameters: a = 7.041 (6), b = 7.612 (6), c = 12.57 (1) Å; α = 104.8 (5), β = 101.5 (5), γ = 103.3 (5)°.

The absence of systematic extinctions again precluded all space groups except $P1$ or $P\bar{1}$. The calculated density, based on a Z value of 1, is 1.892 g/cm^3. The "observed" density was not obtained due to instability of the crystals in the sink–float medium.

The dimensions of the crystal selected for data collection were 0.026 × 0.14 × 0.24 mm. The crystal was aligned along its *b* axis and automated data collection was initiated as described above. With the exception of the scan speed, which was allowed to vary between 1.5 and 15°/min, all conditions were identical, and the system again remained stable. After 1351 intensities had been measured, data collection was terminated.

The data were corrected for *Lp* and absorption (μ = 52.45 cm^{-1}) as described in the previous section.

Structure Determination and Refinement

PTZ–Ni(tfd)$_2$. Calculation of E's yielded E statistics which strongly indicated centrosymmetry; therefore, the space group $P\bar{1}$ was adopted.

A Patterson map was next calculated utilizing a Fourier program known as FORDY,[22] from which the position of the NiS$_4$ portion of the Ni(tfd)$_2$ molecule was obtained. Use of these five atoms as a phasing model in an F_o synthesis yielded all nonhydrogen atomic positions for both molecules.

A full-matrix least-squares refinement was then undertaken using atomic scattering factors for Ni$^+$, S^0, F$^-$, N^0, and C^0 computed from the numerical Hartree–Fock wave functions.[23] The computer program used for all least-squares calculations is known as RFINE.[24] Of the 2246 reflections input, 500 were considered unobserved for they did not meet the requirement: $(C - \text{Bkgd}) > 3.0\sqrt{C + \overline{\text{Bkgd}}})$ where C is the total counts accumulated during the scan and Bkgd is the number of background counts accumulated during the scan. Thus 1746 diffraction maxima were actually used during refinement.

Six least-squares cycles, varying all coordinates and isotropic temperature factors of the 38 atoms, resulted in an R value of 0.131 where R is defined as

$$R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$$

Temperature factors were then converted to their anisotropic form and all parameters were again varied. Due to program limitations all variables could not be varied simultaneously. However, several least-squares runs, varying as many parameters as possible each time, led to a final anisotropic R index of 0.065.

Final atomic coordinates and isotropic equivalents of the anisotropic temperature factors are presented in Table I. Observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material).

POZ–Ni(tfd)$_2$. The E statistics produced an extremely strong indication of centrosymmetry and thus the space group $P\bar{1}$ was adopted. Since the Ni atom was required to occupy a center of symmetry, it was arbitrarily placed at the origin and an F_o map was calculated with all phases positive. From this map the two independent S atoms of the Ni(tfd)$_2$ were easily located. The Ni and two S atoms were then used as a phasing model and the resulting F_o synthesis revealed all atomic positions of both molecules.

A structure of this type can only exist if the central ring of the phenoxazine molecule is disordered since the N and O sites of this ring are equivalent in space group $P\bar{1}$. Thus the full-matrix least-squares refinement was conducted with this position considered as half occupied by N and half by O. This atomic site will be referred to as "ON" in subsequent discussions. Atomic scattering factors for Ni$^+$, S^0, F$^-$, O^0, N^0, and C^0, obtained from the numerical Hartree–Fock wave functions as described in the previous section, were utilized through the refinement. After seven least-squares cycles, varying the positional parameters of the 19 atoms in the asymmetric unit, convergence occurred at an R index of 0.162. Allowing coordinates and isotropic temperature factors to vary simultaneously further lowered R to 0.141.

After converting all temperature factors to their anisotropic form, two additional least-squares cycles were needed to obtain final convergence at an R index of 0.050. In an attempt to investigate the very real possibility that the space group could in fact be $P1$, thus negating the necessity for disorder of the O and N atoms of the phenoxazine molecule, a noncentrosymmetric refinement was carried out. However, no definite conclusions could be reached because of the extremely high correlation coefficients between "centrosymmetrically" related atoms. Final atomic coordinates and isotropic equivalents of the anisotropic temperature factors are given in Table II. Observed and calculated structure factors are available (see paragraph at end of paper regarding supplementary material).

Data on pertinent bond lengths and bond angles for both PTZ–Ni(tfd)$_2$ and POZ–Ni(tfd)$_2$ are collected in Tables III–VI.

Results and Discussion

In PTZ–Ni(tfd)$_2$, the molecules were arranged in an alternating array of two donors and two acceptors (Figure 1). Within the plane of the molecules the sequence alternated between one donor and one acceptor. The stacking axis was very nearly the [111] crystallographic direction. Figure 2

Table I. Final Atomic Coordinates and Isotropic Temperature Factors[a] of the PTZ–Ni(tfd)$_2$ Complex[b]

Atom	*x*	*y*	*z*	*B*, Å^2
		Ni(tfd)$_2$		
Ni	0.1101 (2)	0.1681 (2)	0.4656 (2)	4.29 (5)
S(1)	0.2949 (4)	0.1041 (3)	0.3281 (3)	3.11 (7)
S(2)	0.0734 (4)	0.7701 (3)	0.3943 (3)	3.03 (7)
S(3)	0.0390 (4)	0.3062 (3)	0.3621 (3)	3.05 (7)
S(4)	0.1955 (4)	0.0383 (3)	0.5705 (3)	2.98 (7)
F(1)	0.065 (2)	0.4669 (7)	0.1794 (7)	9.1 (4)
F(2)	0.259 (1)	0.3911 (8)	0.0634 (7)	7.0 (3)
F(3)	0.041 (1)	0.3287 (9)	0.0784 (7)	7.9 (3)
F(4)	0.497 (1)	0.2306 (8)	0.0712 (7)	7.1 (3)
F(5)	0.316 (1)	0.1535 (7)	0.0200 (6)	5.3 (2)
F(6)	0.465 (1)	0.0571 (8)	0.1084 (7)	6.9 (3)
F(7)	0.267 (1)	0.9287 (8)	0.7624 (7)	6.9 (2)
F(8)	0.027 (1)	0.9075 (7)	0.8348 (7)	6.3 (2)
F(9)	0.137 (1)	0.0420 (7)	0.8872 (6)	5.3 (2)
F(10)	0.180 (1)	0.9078 (9)	0.0978 (8)	8.9 (3)
F(11)	0.103 (1)	0.747 (1)	0.1129 (9)	10.8 (4)
F(12)	0.289 (1)	0.780 (1)	0.1792 (7)	8.6 (3)
C(1)	0.277 (2)	0.194 (1)	0.215 (1)	3.1 (3)
C(2)	0.164 (2)	0.286 (1)	0.231 (1)	2.9 (3)
C(3)	0.081 (1)	0.061 (1)	0.704 (1)	2.8 (3)
C(4)	0.040 (2)	0.854 (1)	0.280 (1)	3.0 (3)
C(5)	0.390 (2)	0.161 (1)	0.102 (1)	3.7 (3)
C(6)	0.131 (2)	0.366 (2)	0.137 (1)	4.3 (3)
C(7)	0.124 (2)	0.985 (1)	0.799 (1)	3.6 (3)
C(8)	0.150 (2)	0.822 (1)	0.167 (1)	4.1 (3)
		Phenothiazine		
S	0.2659 (5)	0.4570 (3)	0.4760 (3)	4.39 (9)
N	0.441 (1)	0.730 (1)	0.5738 (9)	3.9 (3)
C(1)	0.463 (2)	0.277 (1)	0.534 (1)	3.2 (3)
C(2)	0.498 (2)	0.804 (1)	0.383 (1)	4.8 (3)
C(3)	0.411 (2)	0.198 (1)	0.727 (1)	4.4 (3)
C(4)	0.279 (2)	0.277 (2)	0.759 (1)	4.9 (3)
C(5)	0.234 (2)	0.356 (1)	0.680 (1)	4.4 (3)
C(6)	0.329 (2)	0.356 (1)	0.568 (1)	3.3 (3)
C(7)	0.458 (2)	0.644 (1)	0.659 (1)	3.3 (3)
C(8)	0.342 (2)	0.648 (1)	0.762 (1)	4.3 (3)
C(9)	0.354 (2)	0.569 (1)	0.849 (1)	4.2 (3)
C(10)	0.481 (2)	0.483 (1)	0.835 (1)	4.1 (3)
C(11)	0.403 (2)	0.524 (1)	0.267 (1)	3.9 (3)
C(12)	0.417 (2)	0.442 (1)	0.354 (1)	3.3 (3)

[a] Anisotropic temperature factors converted to equivalent isotropic. [b] Estimated standard deviations are in parentheses.

Table II. Final Atomic Coordinates and Isotropic Temperature Factors[a] of the POZ–Ni(tfd)$_2$ Complex[b]

Atom	*x*	*y*	*z*	*B*, Å^2
		Ni(tfd)$_2$		
Ni	0	0	0	4.63 (4)
S(1)	0.2228 (3)	0.1752 (3)	0.1552 (2)	3.63 (5)
S(2)	0.2263 (3)	0.1452 (3)	0.9112 (2)	3.62 (5)
C(1)	0.099 (1)	0.178 (1)	0.2596 (6)	3.3 (2)
C(2)	0.900 (1)	0.077 (1)	0.2308 (7)	3.5 (2)
C(3)	0.230 (1)	0.289 (2)	0.3790 (8)	5.0 (2)
C(4)	0.774 (1)	0.065 (2)	0.3131 (8)	4.8 (2)
F(1)	0.3865 (8)	0.4248 (8)	0.3790 (4)	6.8 (2)
F(2)	0.3078 (9)	0.1818 (9)	0.4323 (5)	7.3 (2)
F(3)	0.1321 (8)	0.3783 (9)	0.4448 (4)	7.0 (2)
F(4)	0.7189 (9)	0.2198 (9)	0.3494 (5)	6.8 (1)
F(5)	0.6025 (8)	0.9192 (9)	0.2668 (5)	7.3 (2)
F(6)	0.8682 (8)	0.0323 (8)	0.4063 (4)	6.1 (1)
		Phenoxazine		
C(1)	0.857 (1)	0.472 (1)	0.0588 (9)	4.4 (2)
C(2)	0.718 (2)	0.448 (1)	0.1212 (9)	5.6 (2)
C(3)	0.775 (2)	0.537 (2)	0.237 (1)	6.3 (3)
C(4)	0.978 (2)	0.656 (2)	0.2945 (9)	6.5 (3)
C(5)	0.122 (2)	0.686 (1)	0.2338 (9)	5.4 (2)
C(6)	0.061 (2)	0.592 (1)	0.1158 (8)	4.4 (2)
ON	0.1966 (9)	0.6153 (9)	0.0545 (7)	4.6 (1)

[a] Anisotropic temperature factors converted to equivalent isotropic. [b] Estimated standard deviations are in parentheses.

Table III. Selected Bond Distances (Å) in the PTZ–Ni(tfd)$_2$ Complex[a]

	Ni(tfd)$_2$		
S(1)–C(6)	1.72 (1)	N(1)–C(1)	1.38 (2)
S(1)–C(12)	1.74 (1)	N(1)–C(7)	1.44 (2)
Mean	1.73	Mean	1.41
C(1)–C(2)	1.44 (2)	C(2)–C(3)	1.37 (2)
C(3)–C(4)	1.40 (2)	C(4)–C(5)	1.40 (2)
C(5)–C(6)	1.41 (2)	C(6)–C(1)	1.41 (2)
C(7)–C(8)	1.41 (2)	C(7)–C(12)	1.40 (2)
C(9)–C(10)	1.41 (2)	C(8)–C(9)	1.40 (2)
C(11)–C(12)	1.41 (2)	C(10)–C(11)	1.40 (2)
Mean	1.413	Mean	1.397
	Phenothiazine		
Ni(1)–S(1)	2.126 (4)	S(1)–C(1)	1.720 (1)
Ni(1)–S(2)	2.131 (4)	S(2)–C(4)	1.730 (1)
Ni(1)–S(3)	2.137 (4)	S(3)–C(2)	1.710 (1)
Ni(1)–S(4)	2.129 (4)	S(4)–C(3)	1.700 (1)
Mean	2.131	Mean	1.715
C(1)–C(2)	1.370 (2)	C(5)–F(4)	1.31 (1)
C(3)–C(4)	1.360 (1)	C(5)–F(5)	1.31 (1)
C(1)–C(5)	1.520 (1)	C(5)–F(6)	1.33 (1)
C(2)–C(6)	1.500 (1)	C(6)–F(1)	1.32 (1)
C(3)–C(7)	1.510 (1)	C(6)–F(2)	1.32 (1)
C(4)–C(8)	1.500 (1)	C(6)–F(3)	1.30 (1)
Mean	1.460	C(7)–F(7)	1.34 (1)
		C(7)–F(8)	1.32 (1)
		C(7)–F(9)	1.31 (1)
		C(8)–F(10)	1.30 (1)
		C(8)–F(11)	1.30 (1)
		C(8)–F(12)	1.32 (1)
		Mean	1.315

[a] Estimated standard deviations are in parentheses.

Table IV. Selected Bond Angles (deg) in the PTZ–Ni(tfd)$_2$ Complex[a]

	Ni(tfd)$_2$		
S(1)–Ni–S(4)	87.6 (2)	C(1)–C(5)–F(6)	111.2 (9)
S(1)–Ni–S(3)	91.6 (1)	F(4)–C(5)–F(5)	110.1 (9)
S(3)–Ni–S(2)	89.5 (1)	F(5)–C(5)–F(6)	104.7 (9)
S(2)–Ni–S(4)	91.3 (1)	F(6)–C(5)–F(4)	106.0 (9)
Ni–S(1)–C(1)	104.6 (5)	C(2)–C(6)–F(1)	111.1 (9)
Ni–S(2)–C(4)	104.2 (2)	C(2)–C(6)–F(2)	113.1 (9)
Ni–S(3)–C(2)	104.8 (8)	C(2)–C(6)–F(3)	114 (1)
Ni–S(4)–C(3)	105.3 (4)	F(1)–C(6)–F(2)	103 (1)
S(1)–C(1)–C(5)	115.0 (8)	F(2)–C(6)–F(3)	107.0 (9)
S(1)–C(1)–C(2)	120 (1)	F(3)–C(6)–F(1)	108.1 (9)
C(2)–C(1)–C(5)	125 (1)	C(3)–C(7)–F(7)	110.1 (9)
S(3)–C(2)–C(1)	119.2 (9)	C(3)–C(7)–F(8)	113.4 (9)
S(2)–C(2)–C(6)	116.0 (8)	C(3)–C(7)–F(9)	113.7 (9)
C(1)–C(2)–C(6)	125 (1)	F(7)–C(7)–F(8)	107.1 (9)
S(4)–C(3)–C(4)	119.3 (8)	F(8)–C(7)–F(9)	108.6 (9)
S(4)–C(3)–C(7)	116.7 (7)	F(9)–C(7)–F(7)	103.4 (9)
C(4)–C(3)–C(7)	124.0 (9)	C(4)–C(8)–F(10)	114 (1)
S(2)–C(4)–C(3)	119.6 (8)	C(4)–C(8)–F(11)	103 (1)
S(2)–C(4)–C(8)	114.6 (9)	C(4)–C(8)–F(12)	113 (1)
C(3)–C(4)–C(8)	126 (1)	F(10)–C(8)–F(11)	107.3 (9)
C(1)–C(5)–F(4)	112.9 (9)	F(11)–C(8)–F(12)	106 (1)
C(1)–C(5)–F(5)	111.6 (9)	F(12)–C(8)–F(10)	102 (1)
	Phenothiazine		
N–C(1)–C(6)	125 (1)	N–C(7)–C(8)	118 (1)
N–C(1)–C(2)	116 (1)	C(8)–C(7)–C(12)	118 (1)
C(6)–C(1)–C(2)	118 (1)	C(7)–C(8)–C(9)	121 (1)
C(1)–C(2)–C(3)	119 (1)	C(8)–C(9)–C(10)	120 (1)
C(2)–C(3)–C(4)	122 (1)	C(9)–C(10)–C(11)	121 (1)
C(3)–C(4)–C(5)	121 (1)	C(10)–C(11)–C(12)	118 (1)
C(4)–C(5)–C(6)	118 (1)	C(11)–C(12)–C(7)	122 (1)
C(5)–C(6)–C(1)	121 (1)	C(11)–C(12)–S	115 (1)
C(5)–C(6)–S	116 (1)	C(7)–C(12)–S	123 (1)
C(1)–C(6)–S	123 (1)	C(1)–N–C(7)	121 (1)
N–C(7)–C(12)	124 (1)	C(6)–S–C(12)	102.8 (7)

[a] Estimated standard deviations are in parentheses.

features one donor–acceptor pair, illustrating the thermal ellipsoids associated with each atom. Only very slight deviations from planarity were noted for the NiS_4 portion of

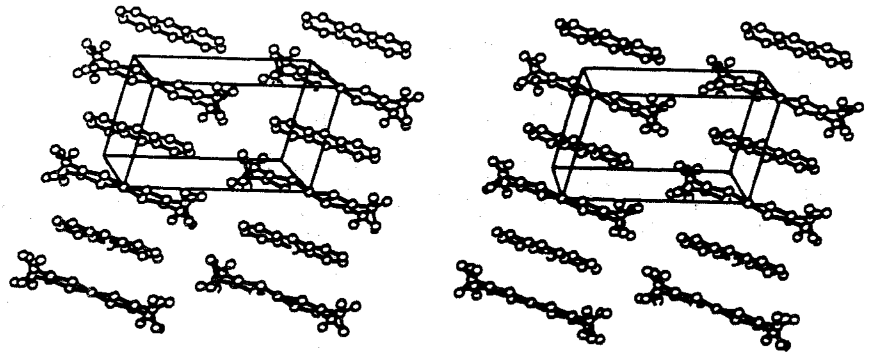

Figure 3. Stereoscopic illustration showing the donor-acceptor stacking sequence in the POZ-$Ni(tfd)_2$ complex. (The origin is at the lower right back corner with +*a* emerging from the paper, +*b* vertical, and +*c* horizontal.)

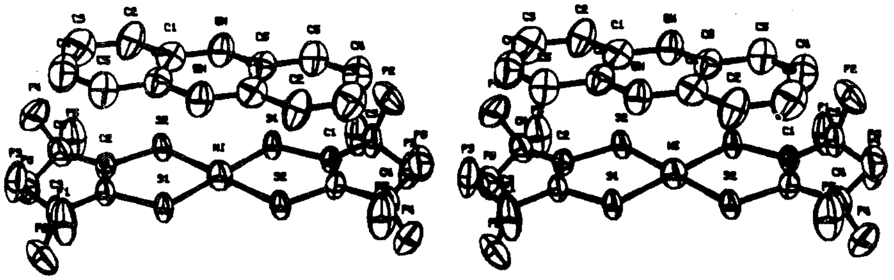

Figure 4. Stereoscopic illustration of one donor-acceptor pair in POZ-$Ni(tfd)_2$ complex.

Table V. Selected Bond Distances (Å) of the POZ-$Ni(tfd)_2$ Complex[a]

	$Ni(tfd)_2$		
Ni-S(1)	2.129 (2)	S(1)-C(1)	1.712 (8)
Ni-S(2)	2.135 (2)	S(2)-C(2)	1.726 (8)
Mean	2.132	Mean	1.719
C(3)-F(1)	1.33 (1)	C(1)-C(3)	1.50 (1)
C(3)-F(2)	1.33 (1)	C(2)-C(4)	1.50 (1)
C(3)-F(3)	1.33 (1)	C(1)-C(2)	1.36 (1)
C(4)-F(4)	1.32 (1)	Mean	1.45
C(4)-F(5)	1.34 (1)		
C(4)-F(6)	1.34 (1)		
Mean	1.332		
	Phenoxazine		
C(1)-ON	1.34 (1)	C(1)-C(2)	1.38 (1)
C(6)-ON	1.35 (1)	C(3)-C(4)	1.43 (2)
Mean	1.345	C(5)-C(6)	1.40 (1)
		C(2)-C(3)	1.37 (1)
		C(4)-C(5)	1.40 (1)
		C(6)-C(1)	1.44 (1)
		Mean	1.40

[a] Estimated standard deviations are in parentheses.

Table VI. Selected Bond Angles of the POZ-$Ni(tfd)_2$ Complex[a]

	$Ni(tfd)_2$		
S(1)-Ni-S(2)	88.65 (7)	C(1)-C(3)-F(2)	112.5 (8)
S(1)-Ni-S(2)*	91.36 (7)	C(1)-C(3)-F(3)	113.2 (8)
Ni-S(1)-C(1)	105.1 (3)	F(1)-C(3)-F(2)	106.0 (8)
Ni-S(2)-C(2)	104.5 (3)	F(2)-C(3)-F(3)	107.7 (8)
S(1)-C(1)-C(3)	114.7 (6)	F(3)-C(3)-F(1)	105.5 (8)
S(1)-C(1)-C(2)	119.5 (6)	C(2)-C(4)-F(4)	113.6 (8)
C(2)-C(1)-C(3)	125.7 (7)	C(2)-C(4)-F(5)	111.8 (7)
S(2)-C(2)-C(4)	115.2 (6)	C(2)-C(4)-F(6)	112.7 (8)
S(2)-C(2)-C(1)	119.5 (6)	F(4)-C(4)-F(5)	106.6 (8)
C(1)-C(2)-C(4)	125.3 (7)	F(5)-C(4)-F(6)	104.7 (8)
C(1)-C(3)-F(1)	111.5 (8)	F(6)-C(4)-F(4)	106.8 (8)
	Phenoxazine		
C(1)-ON-C(6)*	120.9 (7)	C(3)-C(4)-C(5)	121 (1)
ON-C(1)-C(6)	119.6 (9)	C(4)-C(5)-C(6)	117.6 (9)
ON-C(1)-C(2)	120.7 (9)	C(5)-C(6)-C(1)	121.1 (9)
C(2)-C(1)-C(6)	120 (1)	C(5)-C(6)-ON*	119.4 (9)
C(1)-C(2)-C(3)	120 (1)	C(1)-C(6)-ON*	119.6 (9)
C(2)-C(3)-C(4)	120.7 (9)		

[a] Estimated standard deviations are in parentheses. Asterisks refer to symmetry equivalent atoms.

$Ni(tfd)_2$. The orientation and magnitude of the thermal ellipsoids were within the range expected for these types of complexes.[8,25] Particularly notable were the pronounced "out-of-plane" vibrations of most of the atoms and the high degree of thermal motion of the F atoms. POZ-$Ni(tfd)_2$ was found to stack in an alternating DADA sequence, again with the sequence within the molecular planes also alternating (Figure 3). An individual DA pair is shown in Figure 4.

PTZ-$Ni(tfd)_2$. The most striking aspect of the PTZ-$Ni(tfd)_2$ structure is the DDAA stacking sequence, having alternating *pairs* of donors and acceptors (Figure 1). To our knowledge, this is the first reported instance of such a sequence for 1:1 DA complexes. Previously, such "clustering" of adjacent donors or acceptors had been known to occur only in DA stoichiometries other than 1:1[26] or in complexes with segregated stacks of donors and acceptors (*e.g.*, ditoluenechromium-tetracyanoquinodimethane).[27] The other well-established ion radical complex, TMPD-tetrachloroquinone, was found to stack alternately, DADA.[28] In spite of these different stacking sequences, TMPD-TCQ and PTZ-$Ni(tfd)_2$ share noteworthy similarities in physical properties (strong magnetic coupling of the radical spins, intense charge-transfer band in near-ir region).[6a,7,29] The reason for this can be found in the interplanar distances for the phenothiazine complex. The D-A distance is 3.36 Å (defined by the PTZ-sulfur to $Ni(tfd)_2^-$ plane distance), well within the 3.2-3.5 Å reported for interacting DA pairs[30] (3.28 Å in TMPD-tetrachloroquinone[28]), thereby allowing strong interactions between PTZ^+ and $Ni(tfd)_2^-$. On the other hand, the A-A distance (3.83 Å) and D-D distance (varying from 3.4 to 3.9 Å from the donor centers to the edges, due to the folding of the PTZ^+ (*vide infra*)) are too large to allow these interactions to propagate along the stack. It is not surprising, therefore, that although PTZ-$Ni(tfd)_2$ has an intense low-energy charge-transfer band, it also displayed high resistivity (approximately 10^8 ohm cm).[31] Individual DA pairs are essentially isolated from other DA pairs.

The structural parameters for the $Ni(tfd)_2^-$ moiety are best compared to those of $Ni(tfd)_2$ in the neutral $Ni(tfd)_2$-perylene complex[25] and the ionic $Ni(tfd)_2$-tropylium complex.[8] The

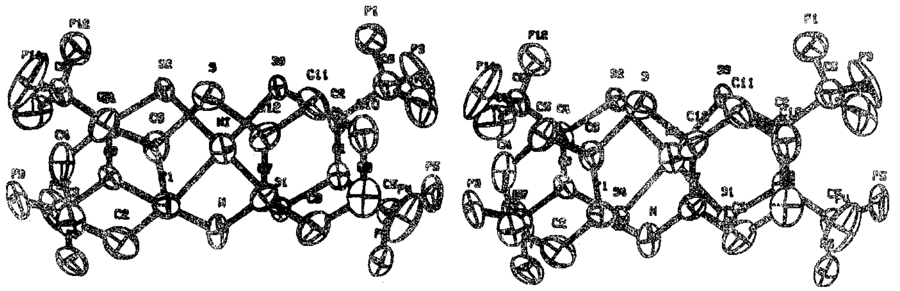

Figure 5. Stereoscopic illustration of one donor–acceptor pair of PTZ–Ni(tfd)$_2$ viewed normal to the plane of Ni(tfd)$_2$.

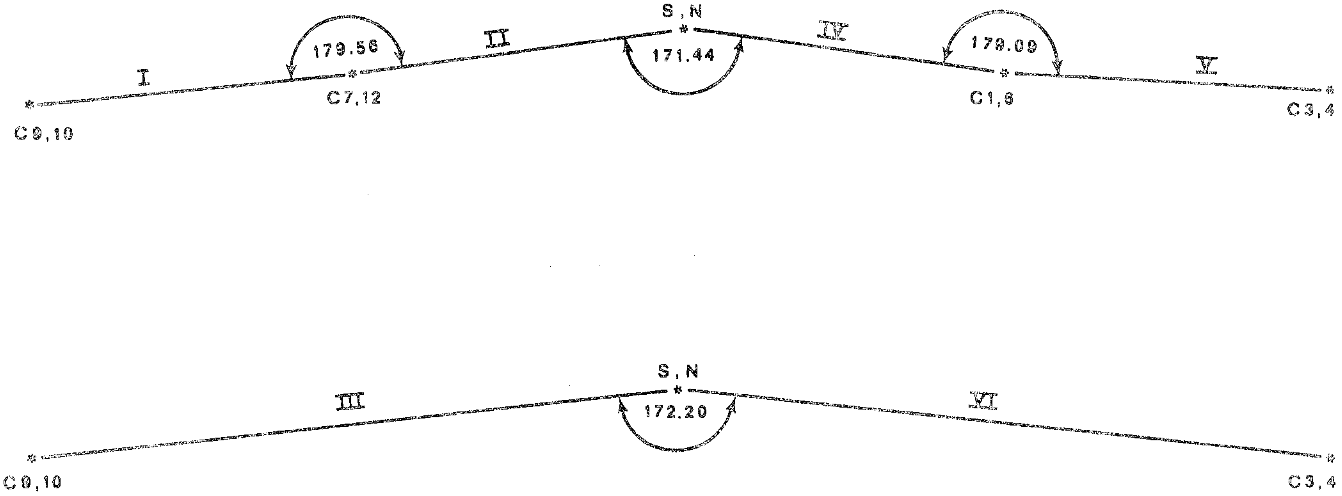

Figure 6. Schematic illustration of the nonplanarity of the phenothiazine cation. See text for significance of Roman numerals.

nickel–sulfur distance (2.131 Å) is longer than that found in the neutral complex (2.122 Å) but very close to that reported in the ionic (tropylium) complex (2.135 Å). It was previously pointed out[8] that lengthening of the Ni–S bond upon reduction of the Ni(tfd)$_2$ species was consistent with the theoretical predictions of Schrauzer and Mayweg.[32] The C–C bond length (1.365 Å) is also consistent with an ionic nickel complex, since reduction of neutral Ni(tfd)$_2$ (C–C bond length 1.38 Å)[25] is expected to lead to increased C–C double bond character and a concomitant shortening of this distance.[33]

The nearly planar halves of the PTZ molecule are not symmetrically disposed with respect to the Ni(tfd)$_2$ plane. A distinct tilt is observable (Figure 2) with half of the PTZ molecule being more nearly parallel to the plane of Ni(tfd)$_2$ than the other. In addition, if the complex is viewed normal to the planes of the molecules as shown in Figure 5, one can see that the PTZ molecule does not symmetrically overlap the Ni(tfd)$_2$ molecule but is slightly shifted to one side.

Structure of the Phenothiazine Cation. The structure of the phenothiazine cation radical is of some interest. Neutral phenothiazine and its derivatives have attracted wide attention due to the pharmacological activity of the latter.[34] Structures of neutral phenothiazine have been reported for free phenothiazine[19] and for the complexed molecule in the (neutral) complex phenothiazine–trinitrobenzene.[35] In both cases a folding of the molecule along the N–S axis was noted. The cation radical was also predicted to be nonplanar.[20,36] Our data support these predictions, for a dihedral angle of approximately 172° was found for PTZ$^+$ in the present case. In addition, although each half of the folded phenothiazine is very nearly planar, there is a small but distinct nonplanarity between the central and outer six-membered rings. As can be seen in Figure 6 (where the angles have been exaggerated for emphasis), "hinging" is apparent between planes I and II and between planes IV and V. This geometry has also been reported for neutral PTZ.[19] If planes I and II were merged by least squares to produce plane III and if planes IV and V were similarly used to form plane VI, the dihedral angle between planes III and VI was 172.2°.

The C–S bond distance (Table III) of 1.73 Å is the expected value for a heterocyclic system in which the C–S bond is shortened by the presence of partial double bonds.[37] The C–S distance in free PTZ is 1.77 Å.[19] The C–S–C angle of 102.8° (Table IV) is larger than that of free PTZ (99.6°) but is nearly the same as that of the PTZ–TNB complex (102°). The mean C–N bond distance of 1.41 Å and the C–N–C angle of 121° are in good agreement with those found in PTZ (1.406 Å and 121.5°, respectively).

POZ–Ni(tfd)$_2$. The alternating DADA stacking sequence of POZ–Ni(tfd)$_2$ is the usual structure of 1:1 donor–acceptor complexes. The structures of the individual ions provided no surprises: the structural parameters for Ni(tfd)$_2^-$ were within experimental error of those found for the same ion in the phenothiazine complex (Tables V and VI) and the phenoxazine cation radical was planar. As in the phenothiazine complex, the donor cation did not lie perfectly symmetrically above the anion (viewed down the molecular axis), and there was a small but significant tilt (1.28°) of the cation from coplanarity with the anion (Figure 4). The most significant aspect of this structure is the donor–acceptor molecular separation of 3.66 Å (the distance from the nickel atom to the least-squares plane of phenoxazine). This distance is significantly outside the optimum donor–acceptor range suggested by Slifkin[38] (3.0–3.4 Å) and slightly longer than the range reported by Bent (2.3–3.6 Å) as leading to donor–acceptor interactions.[39] The long intermolecular distance observed in the present case probably means that charge-transfer interactions are not important in the stabilization of the phenoxazine complex, although such a force is expected to be of importance in the more closely spaced phenothiazine complex. The phenoxazine structure appears to provide a clear rationale for the physical properties of the complex, which are consistent with weak but finite interactions between the donor and acceptor molecules. In this regard, the Curie–Weiss magnetic susceptibility behavior of POZ–Ni(tfd)$_2$ argues against coupling of the unpaired electrons of the donor and acceptor ions, but the esr spectrum (single line, g value approximately the average of those of the cation and anion)[7] suggests that weak exchange interactions do occur between D^+ and A^-. The weak absorption observed in the electronic spectrum of POZ–Ni(tfd)$_2$ in a KBr pellet[7] might then be seen as a charge-transfer transition between weakly overlapping POZ$^+$ and Ni(tfd)$_2^-$.

Summary

The strong intermolecular interactions previously reported[7] between the donor and acceptor radical ions in the PTZ–Ni(tfd)$_2$ complex have been shown to arise from the relative orientation of the ions in the structure and a favorable DA intermolecular separation, which, taken together, ensure appreciable overlap of the donor and acceptor π orbitals. Although the ionic moieties in the analogous POZ–Ni(tfd)$_2$ complex have been shown to have a similarly favorable relative orientation of their molecular π systems, the intermolecular distance (3.66 Å) is apparently too great to allow appreciable overlap of the π systems and a greatly diminished intermolecular interaction occurs.

Registry No. PTZ–Ni(tfd)$_2$, 53142-51-1; POZ–Ni(tfd)$_2$, 53142-52-2.

Supplementary Material Available. Listings of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $5.00 for photocopy or $2.00 for microfiche, referring to code number AIC40410A.

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Preparation and Reactions of μ-Oxido-bis[triphenylphosphinenitrosyliridium(0)]

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The details of the preparation of the complex [Ir(NO)PPh$_3$]$_2$O·C$_6$H$_6$ are reported. Some chemical reactions of this complex are described, limited primarily to those reactions in which the oxygen bridge is retained. Two series of complexes, [IrX(NO)PPh$_3$]$_2$O and [IrX(NO)PPh$_3$]$_2$O·HgX$_2$ (where X = Cl, Br, or I), are reported, as well as 1:1 addition products formed by reaction of the complex [Ir(NO)PPh$_3$]$_2$O with tetracyanoethylene and the p-fluorophenyldiazonium cation.

Introduction

The crystal and molecular structure of the benzene solvate of μ-oxido-bis[triphenylphosphinenitrosyliridium(0)] was the subject of a previous communication;[1] in this paper we now report the preparation and some chemical reactions of this complex. The molecule contains two formally zerovalent iridium atoms which are linked by an oxygen bridge atom and a bent metal–metal bond.

The most common reaction of the compound is one of oxidation of the metal–metal bond by various species giving rise to two square-planar iridium(I) entities linked by the oxygen bridge. These products do not appear to undergo