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Phenyltellurium Halide Complexes of Iron Cyclopentadienyl Dicarbonyl: Synthesis and Molecular Structures of $CpFe(CO)_2TePh$, $CpFe(CO)_2TeBr_2Ph$, $CpFe(CO)_2TeBrPh(\mu\text{-}Br)Br_3TePh$, and $PhTeI_3(C_4H_8O)$

Yu. V. Torubaev, A. A. Pasynskii, and I. V. Skabitskii

Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow, 119991 Russia

E-mail: hansmail@rambler.ru

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Abstract—The bromination of $CpFe(CO)_2TePh$ (**I**) affords the monomeric complex $CpFe(CO)_2TePhBr_2$ (**II**) as the major product and crystals (**III**), being a cocrystallizate of complexes **II** and $CpFe(CO)_2TeBrPh(\mu\text{-}Br)TePhBr_3$ (**IIIA**). Complex **IIIA** contains a $PhTeBr_3$ molecule, which is weakly bound because of the lone electron pair (LEP) of the bridging bromine atom of molecule **II**. An analogous weak interaction with the LEP of oxygen in tetrahydrofuran (Te···O 2.893 Å) is observed in the $PhTeI_3$(THF) adduct (**IV**), which is a dimer with two bridging iodine atoms and can be obtained by the crystallization of $PhTeI_3$ from THF. According to the X-ray diffraction data, the Fe–Te distances in compounds **II** and **IIIA** (on the average, 2.5 Å) differ slightly and are similarly shortened by 0.2 Å compared to the sum of the covalent radii of iron and tellurium. The secondary interactions Te···halide and Te···π system of the phenyl ligand are discussed.

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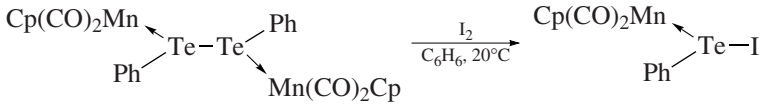
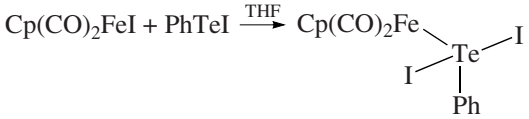
INTRODUCTION

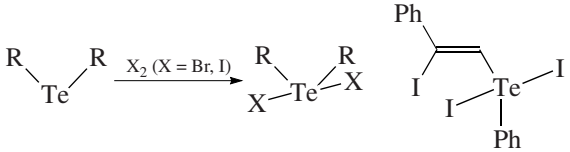
We recently showed that the reaction of molecular iodine with $[CpMn(CO)_2]_2(\mu\text{-}Ph_2Te_2)$ afforded $CpMn(CO)_2(PhTeI)$; i.e., the metal–tellurium bond is retained upon the Te–Te bond cleavage and tellurium–halogen bond formation [1]



At the same time, we obtained the $CpFe(CO)_2TeI_2Ph$ complex by the insertion of PhTeI into the Fe–I bond in $CpFe(CO)_2I$ [1]



This complex contains the TeI_2Ph ligand analogous to those observed in diorganotellurium diiodides $RTeI_2Ph$, which are formed upon the oxidative addition of halogens to tellurium ethers R_2Te [2]



It could be assumed that the halogenation of $CpFe(CO)_2TePh$ (**I**) [3] with one equivalent of Br_2 would proceed at the tellurium atom without the Fe–Te bond cleavage to form the corresponding dibromide $CpFe(CO)_2TeBr_2Ph$.

EXPERIMENTAL

All procedures on the synthesis and isolation of the complexes were carried out under pure argon in anhydrous solvents. IR spectra were recorded on a Specord 75 IR spectrophotometer (KBr pellets). Commercial $[CpFe(CO)_2]_2$, Ph_2Te_2, and Br_2 were used without additional purification.

Synthesis of $CpFe(CO)_2TeBr_2Ph$ (II) and the cocrystallizate of II with $CpFe(CO)_2TeBrPh(\mu\text{-}Br)Br_3TePh$ (III). A solution of $[CpFe(CO)_2]_2$ (0.18 g, 0.5 mmol) and Ph_2Te_2 (0.2 g, 0.5 mmol) in benzene

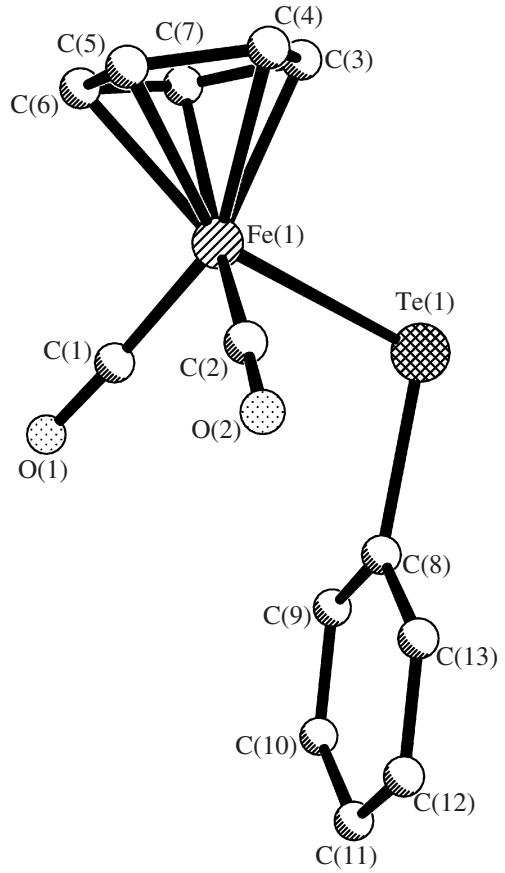


Fig. 1. Molecular structure of complex **I** (selected bond lengths: Te(1)–Fe(1) 2.617(1), Te(1)–C(8) 2.139(8), O(1)–C(1) 1.140(4), and O(2)–C(2) 1.145(4)Å; bond angle: C(8)Te(1)Fe(1) 102.5(2)°).

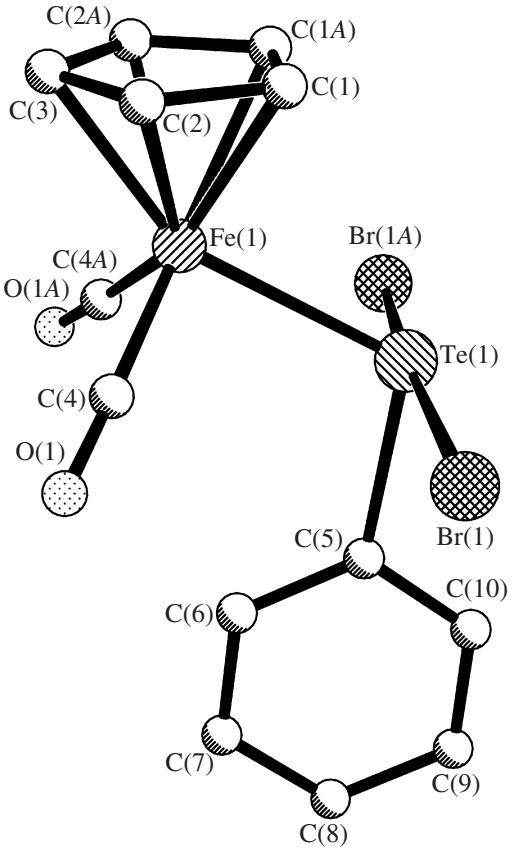


Fig. 2. Molecular structure of complex **II** (selected bond lengths: Fe(1)–Te(1) 2.499(3), Br(1)–Te(1) 2.7046(14), Br(1)–Te(1)$^{\#1}$ 2.7046(14), and Te(1)–C(5) 2.121(15) Å; bond angles: C(5)Te(1)Fe(1) 109.4(4)°, Fe(1)Te(1)Br(1)$^{\#1}$ 94.24(3)°, C(5)Te(1)Br(1) 87.33(4)°, and Br(1)$^{\#1}$Te(1)Br(1) 171.11(7)°).

(30 ml) was refluxed for 3 h. During this time, compound **I** was mainly formed [3]. Compound **I** was characterized by IR spectral data and TLC. Bromine (0.05 ml, 1 mmol) in petroleum ether (10 ml) was added with magnetic stirring to the brown-green reaction mixture cooled to room temperature. Petroleum ether (10 ml) was added to the dark yellow solution formed. The mixture was filtered, the resulting solution was concentrated in a vacuum of a water-jet pump until turbidity appeared, and the residue was kept for 12 h at –10°C. The yellow crystals formed were filtered off, washed with hexane, and dried in vacuo. The yield was 0.15 g (28%).

For $C_{13}H_{10}Br_2FeO_2Te$ (II)		
anal. calcd., %:	C, 28.84;	H, 1.86.
Found, %:	C, 27.31;	H, 1.78.

IR (KBr), ν(CO), cm^{-1}: 2035 s, 1995 s.

Yellow single crystals of compound **II** suitable for X-ray diffraction analysis grew after petroleum ether was carefully deposited on the filtered mother liquor. The bulk of formed crystals **II** contained a small amount of slightly larger rhombi of cocrystallizate **III**, which were also studied by X-ray diffraction analysis (probably, their presence underestimates the carbon content).

Synthesis of $PhTeI_3(C_4H_8O)$ (IV). Dark orange prismatic crystals of adduct **IV** suitable for X-ray diffraction analysis were formed on cooling of a saturated solution of $PhTeI_3$ in a THF–heptane (1 : 1) mixture.

X-Ray diffraction analysis. The crystals of compound **I** suitable for X-ray diffraction analysis were obtained by the recrystallization of the product synthesized according to a described procedure [3] from a benzene–heptane mixture. The crystallographic data and refinement parameters for structures **I–IV** are collected in the table. Structures **I–IV** were determined by a direct method and refined by the least-squares method for F^2 in the anisotropic (isotropic for H atoms) approximation using the SHELXTL program package [4]. The positions of the H atoms were calculated geometrically. Selected bond lengths and bond angles for complexes **I–IV** are

Selected crystallographic data for complexes **I–IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Empirical formula	$C_{13}H_{10}FeO_2Te$	$C_{13}H_{10}Br_2FeO_2Te$	$C_{38}H_{31}Br_7Fe_2O_4Te_3$ (C_6H_6 $C_{32}H_{25}Br_7Fe_2O_4Te_3$)	$C_{10}H_{13}I_3OTe$
Diffractometer	Bruker APEX III CCD			
FW	381.66	541.48	1605.50	657.50
Radiation (λ, Å),	MoK_α, (0.71073)			
Temperature, K	296(2)	100(2)	150(2)	260(2)
Space group	$P2_1/c$	*P*nma	*P*–1	$P2_1/n$
a, Å	9.6899(17)	12.850(5)	8.5192(9)	11.9172(15)
b, Å	11.676(2)	9.264(2)	12.0217(12)	8.8028(11)
c, Å	11.802(2)	12.579(4)	23.709(2)	15.2045(19)
α, deg	90	90	76.851(2)	90
β, deg	103.546(3)	90	89.099(2)	99.248(2)
γ, deg	90	90	74.492(2)	90
V, Å^3	1298.2(4)	1497.5(8)	2275.8(4)	1574.3(3)
Z	4	4	2	4
ρ_{calcd}, g/cm^3	1.953	2.402	2.343	2.774
μ, mm^{-1}	3.350	8.246	8.704	7.751
F(000)	728	1008	1488	1168
θ range, deg	2.16–29.00	2.27–28.00	1.77–29.00	2.02–29.00
Scan mode	ω			
Total number of reflections	14024	9114	25271	13052
Независимых отражений (N_1)	3443 (R_{int} = 0.0340)	1918 (R_{int} = 0.1360)	12078 (R_{int} = 0.0659)	4141 (R_{int} = 0.0912)
Reflections with $I > 2\sigma(I)$ (N_2)	2516	1116	7074	2424
Number of refined parameters	149	101	481	136
Goodness-of-fit (F^2)	1.010	0.943	0.941	0.952
R_1 for N_2	0.0332	0.0665	0.0506	0.0528
wR_2 % for N_1	0.0841	0.2088	0.1003	0.1165
$\Delta\rho_{max}/\Delta\rho_{min}$, *e* Å^{-3}	1.329/–0.658	2.010/–1.155	1.073/–1.211	1.686/–1.274

given in the figure captions (Figs. 1–4). The positions of the Cp ligand and TePh group in structure **I** are disordered with unequal site occupancies. The distances and angles in the molecule with the highest occupancy are discussed and, correspondingly, presented in the figure caption to Fig. 2. The atomic coordinates and other parameters for structures **I**–**IV** were deposited with the Cambridge Structural Database (nos. 708821 (**I**), 707629 (**II**), 706955 (**III**), and 694366 (**IV**); http://www.ccdc.cam.ac.uk/data_request/cif).

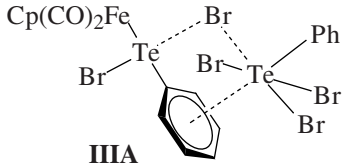
RESULTS AND DISCUSSION

The reaction between compound **I** and Br_2 in benzene at room temperature afforded yellow crystals of monomeric complex **II** and dark yellow crystals of compound **III** as an insignificant admixture to compound **II**. The crystals of compound **III** contain the solvate benzene molecule and the cocrystallizate of molecule **II** and the adduct of complex **II** with the $PhTeBr_3$ molecule ($CpFe(CO)_2TeBrPh(\mu\text{-}Br)Br_3TePh$ (**IIIA**))

$$[Cp(CO)_2Fe]_2 + Ph_2Te_2 \xrightarrow[C_6H_6]{80^\circ C} \underset{\mathbf{I}}{Cp(CO)_2Fe{-}TePh} \xrightarrow[C_6H_6]{Br_2} \underset{\mathbf{II}}{Cp(CO)_2Fe(Br)Te(Br)Ph}$$

The formation of $PhTeBr_3$ composing **IIIA** is probably due to the presence of an insignificant amount of unreacted Ph_2Te_2 in the reaction mixture. The unreacted Ph_2Te_2 reacts in the bromination along with compound **I**

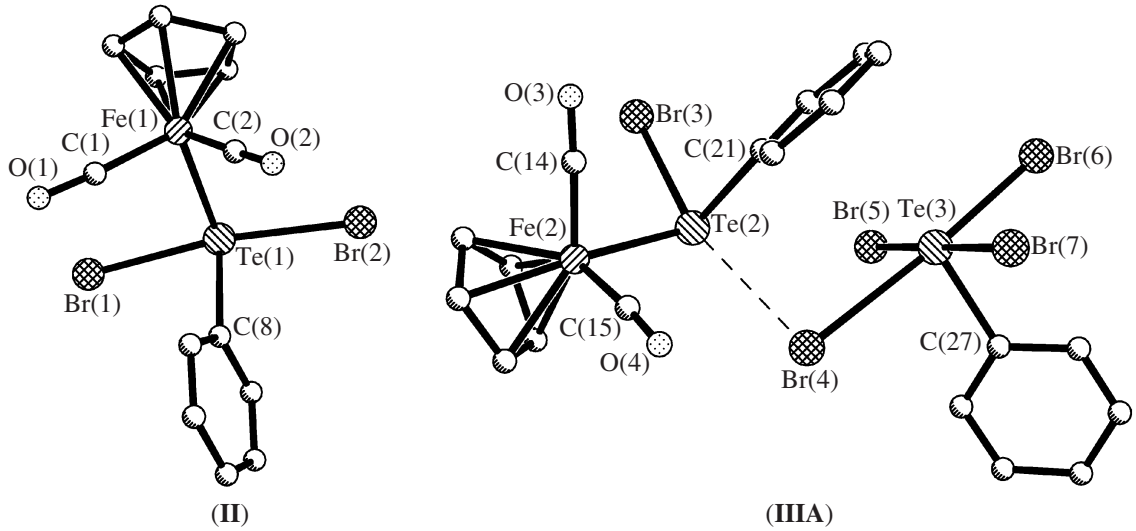
$$Ph_2Te_2 \xrightarrow[C_6H_6]{Br_2} PhTeBr_3$$



IIIA

The IR spectrum of compound **II** exhibits two strong bands in the region of stretching vibrations of the carbonyl groups (2035 and 1995 cm^{-1}), which are also observed in the spectra of analogous complexes (η_4-C_4Me_4)$Co(CO)_2TeBrIPh$ (2040, 2000 cm^{-1}) [5], $CpFe(CO)_2TeI_2Ph$ (**V**) (2035, 1990 cm^{-1}) [1], and $CpFe(CO)_2I$ (2035, 2000 cm^{-1}) [6] and are shifted by 15 cm^{-1} to the high-frequency region compared to the starting compound **I** (2018, 1976 cm^{-1}) [3].

According to the X-ray diffraction data, the Fe–Te bond is retained in complexes **II** and **III** (Figs. 2, 3). This bond is shortened to 2.499(3) and 2.5091(11) Å in structures **II** and **III**, respectively, compared to 2.617(1) Å in the starting complex **I** (Fig. 1), whose geometry resembles that found for the isoelectronic complex (η_4-C_4Me_4)$Co(CO)_2TePh$ (Co–Te 2.5848(11) Å) [7]. However, in spite of the differences in the molecu-



(**II**) (**IIIA**)

Fig. 3. Structures **II** and **IIIA** in cocrystallizate **III** (selected bond lengths: Fe(1)–Te(1) 2.5217(12), Te(1)–Br(1) 2.7146(9), Te(1)–Br(2) 2.7307(9), Te(1)–C(8) 2.136(7), Fe(2)–Te(2) 2.5091(11), Te(2)–C(21) 2.115(7), Te(2)–Br(3) 2.599(1), Te(2)–Br(4) 3.034(1), Te(3)–C(27) 2.132(7), Te(3)–Br(4) 2.9647(8), Te(3)–Br(5) 2.7104(10), Te(3)–Br(6) 2.5797(9), and Te(3)–Br(7) 2.6441(9) Å; bond angles: C(8)Te(1)Fe(1) 110.5(2)°, Fe(1)Te(1)Br(1) 95.90(4)°, C(8)Te(1)Br(1) 88.26(19)°, Br(1)Te(1)Br(2) 171.28(3)°, C(21)Te(2)Fe(2) 106.31(19)°, and Fe(2)Te(2)Br(3) 97.43(3)°).

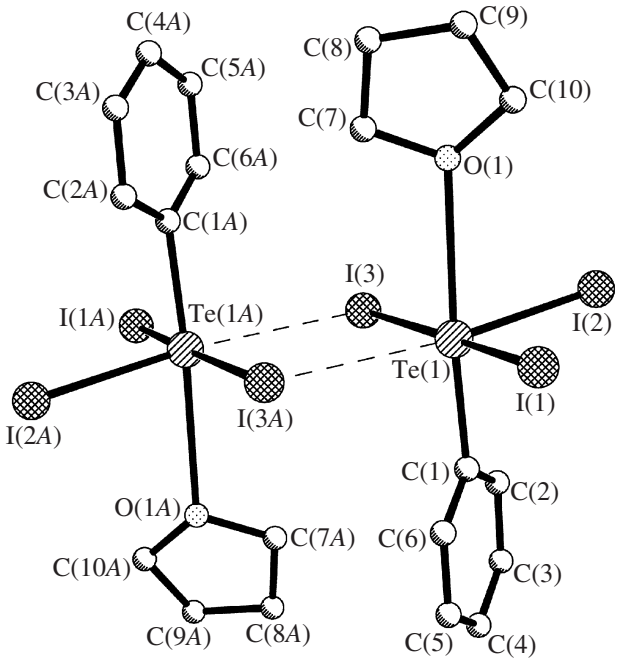


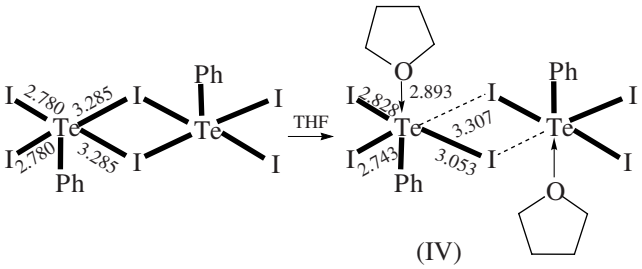
Fig. 4. Molecular structure of complex **IV** (selected bond lengths: Te(1)–C(1) 2.178(10), Te(1)–I(1) 2.8279(11), Te(1)–I(2) 2.7424(9), Te(1)–I(3) 3.0528(10), Te(1)–O(1) 2.894(1), and Te(1)–I(3*A*) 3.307(1) Å; bond angles: C(1)Te(1)I(2) 95.4(3)°, C(1)Te(1)I(1) 92.5(3)°, I(2)Te(1)I(1) 93.93(3)°, C(1)Te(1)I(3) 89.5(3)°, I(2)Te(1)I(3) 90.65(3)°, Te(1)I(3)Te(1*A*) 91.66(3)°, and O(1)Te(1)C(1) 176.23(3)°).

lar structures of complexes **I**, **II**, and **IIIA**, the Fe–Te distances in them differ slightly and are close to the Fe–Te distance (2.5305(17) Å) in similar iodine-containing complex **V** [1]. Chiefly, all these distances are similarly strongly shortened (by 0.2 Å) compared to the sum of the covalent radii of Fe and Te (1.34 and 1.38 Å [8]).

Note that the Te(1), Fe(1), C(3)(Cp), and C(5)(Ph)–C(10)(Ph) atoms in molecule **II** lie in the *m* plane, due to which the Te–Br distances are equivalent and equal to 2.7046(14) Å, unlike those in cocrystallizate **III**, where analogous distances differ and are elongated to 2.7146(9) and 2.7307(9) Å.

In complex **IIIA**, two distances Te(2,3)–(μ-Br(4) are close (on the average, 3.000(1) ± 0.035 Å), which is substantially longer than 2.644–2.745 Å in the $PhTeBr_4^-$ anion [9]. Thus, complex **IIIA** cannot be considered as the ionic complex $[CpFe(CO)_2TeBrPh]^+[PhTeBr_4]^-$. It is most likely that the bridging coordination of the bromine atom is comparable with the weak interaction between the tellurium atom and the LEP of oxygen in the tetrahydrofuran molecule (Te(1)–O(1) 2.894 Å) in dimeric adduct **IV** with the bridging iodine atoms (Fig. 4). We isolated adduct **IV** by the crystallization of $PhTeI_3$ from a THF–heptane (1 : 1) mixture.

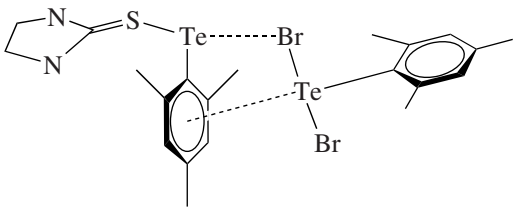
Analogous dimerization was observed in the crystalline complex $[trans\text{-}PhTeI_3]_2$ (**VI**) [10]. However, the Te–(μ-I) distances in dimer **IV** (3.307(1)–3.053(1) Å) somewhat differ from 3.285 Å in complex **IV**.



(IV)

It is interesting that the THF molecule in **IV** is coordinated perpendicularly to the plane of the iodide ligands in the *trans* position to the phenyl ligand, which makes the tellurium atom hexacoordinate. In all other described cases, the π-donor ligand coordinates in the plane of the halide atoms in the *trans* position to one of them, and the coordination number of Te is five. Probably, in dimer **IV** the LEP of tellurium interacts with the iodide bridge arranged farther according to the charge-transfer complex type.

Another manifestation of the stereochemical activity of the LEP of the tellurium atom can be the parallel arrangement of the $TeBr_4$ planes of the $PhTeBr_3$ fragment and the phenyl ligand at the tellurium atom in the adjacent $CpFe(CO)_2TeBr_2Ph$ fragment in molecule **IIIA** (Fig. 3), the distance Te···center of the Ph ring being not too long (on the average, 3.5 Å). This assumption on the weak interaction between the LEP of the tellurium atom in $PhTeBr_3$ and the π system of the phenyl ligand in **II** is analogous to the earlier assumption for the MesTeX(μ-X)TeMes(Etu) complex (X = Br, I; Etu is ethylenethiourea) [11]



At the same time, it cannot be excluded that this structure is only a consequence of the packing effects.

Thus, it is shown that the phenyltelluride group bound in the transition metal complex is halogenated in the same manner as diorganyl tellurides, the sharp shortening of the metal–tellurium bond is retained, and diverse secondary interactions of the charge-transfer complex type are observed.

ACKNOWLEDGMENTS

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