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Synthesis and Spectra of *cis*-$[NCl(phen)_2Tc]Cl{\cdot}H_2O$ and *cis*-$[NCl(phen)_2Tc]PF_6$ and Considerations of Their Structural Distortions

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Received April 19, 1991

In crystalline *cis*-$[NCl(phen)_2Tc]PF_6$ the complex ion exhibits a pseudo-2-fold symmetry axis that gives rise to a reproducible enantiomeric disorder (85%/15%). Left untreated, this yields bond distance inaccuracies in the X-ray structure solution such that the $Tc{\equiv}N$ bond appears to lengthen by 0.15 Å. In *cis*-$[NCl(phen)_2Tc]Cl{\cdot}H_2O$ no pseudosymmetry is present and the complex (I) crystallizes in the space group $P\bar{1}$ (No. 2, triclinc) with the cell parameters a = 11.4148 (8) Å, b = 12.332 (1) Å, c = 8.5835 (6) Å, α = 101.244 (8)°, β = 107.363 (6)°, γ = 80.326 (7)°, Z = 2, and R = 0.046. The same complex (II) in *cis*-$[NCl(phen)_2Tc]PF_6$ crystallizes in $P2_1/a$ (No. 14, monoclinic) with the cell parameters a = 13.806 (3) Å, b = 12.587 (2) Å, c = 14.880 (3) Å, β = 112.74 (2)°, Z = 4, and R = 0.043. Correct crystallographic solutions yield bond lengths in I and II that are identical within experimental error. Bond lengths in I and II, respectively: $Tc{\equiv}N$, 1.603 (5) and 1.593 (5) Å; Tc—Cl, 2.412 (2) and 2.405 (2) Å. Nevertheless, packing forces generate a true bending distortion between I and II involving the orientation of the phenanthroline ligands. In solution, both complexes generally exhibit nearly identical properties, but occasional differences are noted. These results have implications for shape recognition of nucleic acid structures by transition-metal complexes with large aromatic rings.

The existence of "bond stretch" isomers, which have been defined as structurally identical species but with significantly different bond lengths, is now dubious. Most reports have involved oxo complexes with d^2 electronic configurations[1-3] but also include d^1 compounds[4] with a $[W{=}O]^{3+}$ core,[5] some seven-coordinate, d^0 complexes with varying M—S bonds (M = Nb or Ta),[6] and a suggestion that similar nitrido complexes differ substantially in their $Re^V{\equiv}N$ bond lengths.[7-9] The oldest example of this class of compounds[1,2] has recently been shown to derive from a crystallographic artifact arising from doping with a complex of similar shape and charge.[10,11] Electronic mechanisms explaining bond stretch isomers through either energy-state crossing or second-order Jahn–Teller effects[12] have been shown unlikely by ab initio calculations.[13] Herein we report on the structures of *cis*-$[NCl(phen)_2Tc]^+$ as two different salts and show that a true distortional difference between the complex (I) in the chloride salt and the same species (II) in the hexafluorphosphate salt leads to a pseudo-2-fold symmetry in II that results in a reproducible enantiomeric disorder. Incorrectly treating this disorder leads to an apparent bond stretch pair in complexes with identical bond lengths such that the innacurate bond length differences coincidentally correspond exceedingly well with those predicted by Jean.[12]

Experimental Section

Synthesis. *cis*-$[NCl(phen)_2Tc]Cl{\cdot}H_2O$ was prepared by dissolving 100 mg of $(n\text{-}Bu_4N)[NCl_4Tc]$[14] in 10 mL of methanol. Addition of 200 mg of 1,10-phenanthroline followed by 2 h of stirring yielded a reddish-yellow solution, which precipitated upon addition of diethyl ether. After cooling, a microcrystalline product was filtered and washed with $CHCl_3$ and diethyl ether. Yield: 95%. Elemental Anal. Calcd for $H_{18}C_{24}N_5OCl_2Tc$: H, 3.23; C, 51.26; N, 12.45. Found: H, 3.26; C, 51.01; N, 12.45. IR (cm^{-1}): in KBr pellet 1626 (s), 1517 (vs), 1428 (vs), 1071 ($\nu_{Tc{\equiv}N}$, s), 1054 ($\nu_{Tc{\equiv}N}$, s), 849 (vs), 780 (m), 722 (vs), 646 (m); in Nujol (calibrated with Nujol 1377 peak) 1341, 1314, 1260, 1222, 1213, 1147, 1111, 1069 ($\nu_{Tc{\equiv}N}$, s), 1056 ($\nu_{Tc{\equiv}N}$, s); dissolved in formamide 1225, 1213, 1149, 1109, 1067, 1053. UV–vis [λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)]: in methanol 274 (4.04×10^4), 351 (sh), 414 (2.8×10^3), 550 (sh); in CH_3CN 416 nm (2.85×10^3); solid state 325, 428, 480. $\mu_{eff} = 0.6\ \mu_B$. HPLC: μC_{18}, 20% CH_3CN/CH_3OH, 0.6 mL/min, $k' = 0.9$.

The compound $[NCl(phen)_2Tc]PF_6$ was initially prepared by mixing 100 mg of $(Ph_4As)[NCl_4Tc]$[14] with 100 mg of *o*-phenanthroline in 10 mL of water. After stirring for 1 h, the mixture was filtered and washed with water. The combined filtrate was washed with $CHCl_3$ and diethyl ether. After precipitating with NH_4PF_6(aq), the product was further purified on a Sephadex-CM ion-exchange column by elution with 0.05 M ammonium formate to remove $[AsPh_4]^+$ and 0.15 M ammonium formate to obtain the product. Precipitation was induced as above and the compound recrystallized from acetone. Yield: 75%. Elemental Anal. Calcd for $H_{16}C_{24}N_5F_6ClPTc$: H, 3.13; C, 40.72; N, 9.89. Found: H, 2.54; C, 40.18; N, 9.41. IR (cm^{-1}): in KBr pellet 1632 (s), 1518 (s), 1426 (vs), 1063 ($\nu_{Tc{\equiv}N}$, m), 1046 ($\nu_{Tc{\equiv}N}$, s), 846 (vs), 719 (vs), 648 (m), 556 (vs); in Nujol 1066 ($\nu_{Tc{\equiv}N}$, m), 1050 ($\nu_{Tc{\equiv}N}$, s). UV–vis [λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)]: in acetone 352 (sh), 418 (3.35×10^3), 581 (sh); in CH_3CN 416 (3.17×10^3); solid state 319, 402, 479. $\mu_{eff} = 1.15$. This compound was also prepared by dissolving 20 mg of *cis*-$[NCl(phen)_2Tc]Cl{\cdot}H_2O$ in 1 mL of methanol and reprecipitating it with NH_4PF_6 in methanol. Crystals were obtained from acetone. Except where noted, the solution properties were identical to those of *cis*-$[NCl(phen)_2Tc]Cl{\cdot}H_2O$.

Crystal Structures. A single crystal of $[NCl(phen)_2Tc]Cl{\cdot}H_2O$ (grown by slow evaporation of a methanol solution) was mounted on a glass fiber and placed in the beam of a Rigaku AFC5R diffractometer. Solution and refinement procedures and pertinent crystal and refinement data are given in Table I. Atomic positions are listed in Table II.

A single crystal of $[NCl(phen)_2Tc]PF_6$ prepared by the first synthetic method was selected, and data were collected with Mo Kα radiation. Crystallographic data are given in Table I. Space group assignment was based on the systematic absences of $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$. Two additional crystals of $[NCl(phen)_2Tc]PF_6$ were prepared from separate batches of $[NCl(phen)_2Tc]Cl{\cdot}H_2O$ dissolved in a minimum of methanol and reprecipitated by addition of concentrated NH_4PF_6 in methanol. Data were collected with Cu Kα radiation. Initial structure solutions of all three crystals proceeded as above and yielded a long $Tc{\equiv}N$ bond (1.754 (6) Å) and a somewhat short Tc—Cl length (2.366 (5) Å) with R factors ≤0.061. While enantiomeric disorder was suspected early, a number of attempted solutions in which one or both of the disordered atoms (Cl* and N1*) were placed in calculated positions (at Tc—N1* = 1.60 Å along the Tc—Cl axis and Tc—Cl* = 2.41 Å along Tc—N1)

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(1) Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *Chem. Commun.* **1971**, 655–656.

(2) Cotton, F. A.; Diebold, M. P.; Roth, W. *Inorg. Chem.* **1987**, *26*, 2848–52.

(3) Wieghardt, K.; Bakes-Dahmann, G.; Holzbach, W. *Z. Anorg. Allg. Chem.* **1983**, *499*, 44–58.

(4) Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594–1602.

(5) Weighardt, K.; Backes, G.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 777–778.

(6) Gibson, V. C.; Kee, T. P.; Shaw, A.; Williams, D. N. *Abstracts of Papers*; 199th National Meeting of the American Chemical Society; Boston, MA, April 22–27, 1990; American Chemical Society: Washington, DC, 1990; INOR 134.

(7) Haymore, B. L.; Goddard, W. A.; Allison, J. N. *Proc. Int. Conf. Coord. Chem.* **1984**, *23*, 535.

(8) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.

(9) Forsellini, E.; Casellato, U.; Graziani, R.; Magon, L. *Acta Crystallogr., Sect. B.* **1982**, *B38*, 3081.

(10) Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 1437.

(11) Desrochers, P. J.; Nebbesy, K. W.; LaBarre, M. J.; Lincoln, S. E.; Loehr, T. M.; Enemark, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 9193–9200.

(12) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 4506–4516.

(13) Song, J.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 4433–4437.

(14) Baldas, J.; Boas, J. F.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 2395–2400.

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Table I. Crystallographic Data for *cis*-[NCl(phen)$_2$Tc]Cl·H$_2$O and *cis*-[NCl(phen)$_2$Tc]PF$_6$[a,c]

formula	$C_{24}H_{18}N_5Cl_2OTc$	$C_{24}H_{16}N_5PF_6ClTc$
fw	562.25	653.74
space group, cryst syst	triclinic, $P\bar{1}$ (No. 2)	monoclinic, $P2_1/a$ (No. 14)
cell constants		
a, Å	11.4148 (8)	13.806 (3)
b, Å	12.332 (1)	12.587 (2)
c, Å	8.5835 (6)	14.880 (3)
α, deg	101.244 (3)	112.74 (2)
β, deg	107.363 (1)	
γ, deg	80.326 (6)	
cell vol, Å^3	1123.1 (2)	2385 (2)
Z (fw/unit cell)	2	4
radiation source (graphite monochromated); λ, Å	Cu Kα; 1.541 78	Mo Kα; 0.710 69
d_{calcd}, g/cm^3	1.66	1.82
μ, rel trans factors, cm^{-1}	76.60	8.27
$R = \sum(\lvert F_o\rvert - \lvert F_c\rvert)/\sum\lvert F_o\rvert$	0.046	0.043
$R_w{}^b = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum\lvert w(F_o)^2\rvert]^{1/2}$	0.071	0.057

[a] T = 23 (1) °C. Reflections with $I_o > 3\sigma(I_o)$ were retained as observed and used in the solution and refinement of the structure. Three standard reflections were monitored with a limit of 0.2% variation. Function minimized $\sum w(|F_o| - |F_c|)^2$. [b] Weighting scheme: $w = 4(F_o)^2[\sigma^2/(F_o)^2]^2$. [c] All calculations were performed by using the TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corp., 1985. Neutral-atom scattering factors and anomalous dispersion effects were included in F_c;[33] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[35] No decay correction was necessary. An empirical absorption correction was applied. Tc and the majority of other atoms were located by direct methods, and the remaining atoms were found from difference Fourier maps.[35,36] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealized positions (C–H = 0.95 Å), with thermal parameters 20% greater than the B_{eq} value of the atoms to which they were bonded. Refinement was by full-matrix least squares.

Table II. Crystallographic Coordinates and Isotropic Thermal Parameters for Atoms in [NCl(phen)$_2$Tc]Cl·H$_2$O

atom	x	y	z	B,[a] Å^2
Tc	0.74726 (4)	0.81752 (4)	0.34648 (5)	2.04 (2)
Cl1	0.4145 (3)	0.5892 (3)	0.0579 (4)	8.3 (2)
Cl2	0.8870 (2)	0.8596 (2)	0.6175 (2)	4.01 (8)
O1	0.4225 (3)	0.5981 (3)	0.4249 (4)	1.5 (1)
N1	0.6211 (5)	0.8174 (5)	0.3926 (7)	3.1 (2)
N2	0.8109 (5)	0.6443 (4)	0.3428 (6)	2.4 (2)
N3	0.9316 (5)	0.7847 (4)	0.2563 (7)	2.7 (2)
N4	0.6739 (4)	0.7960 (4)	0.0857 (6)	2.1 (2)
N5	0.7289 (5)	0.9827 (4)	0.2978 (6)	2.4 (2)
C1	0.7506 (7)	0.5756 (6)	0.3829 (8)	3.0 (3)
C2	0.7891 (8)	0.4618 (6)	0.371 (1)	3.7 (3)
C3	0.8903 (8)	0.4180 (6)	0.320 (1)	3.8 (3)
C4	0.9557 (6)	0.4882 (6)	0.2785 (8)	3.0 (3)
C5	1.0642 (7)	0.4483 (6)	0.223 (1)	4.0 (3)
C6	1.1256 (7)	0.5201 (7)	0.182 (1)	4.0 (3)
C7	1.0829 (6)	0.6349 (6)	0.1891 (8)	3.2 (3)
C8	1.1388 (6)	0.7134 (8)	0.143 (1)	4.0 (3)
C9	1.0934 (7)	0.8189 (7)	0.159 (1)	4.2 (4)
C10	0.9898 (6)	0.8552 (6)	0.215 (1)	3.5 (3)
C11	0.9763 (5)	0.6763 (5)	0.2450 (8)	2.5 (3)
C12	0.9122 (6)	0.6017 (5)	0.2889 (7)	2.3 (2)
C13	0.6435 (6)	0.7019 (5)	−0.0156 (8)	2.5 (3)
C14	0.6019 (6)	0.6976 (6)	−0.1829 (8)	3.2 (3)
C15	0.5893 (6)	0.7926 (6)	−0.2532 (8)	3.0 (3)
C16	0.6196 (6)	0.8925 (6)	−0.1505 (8)	2.7 (3)
C17	0.6057 (6)	0.9968 (6)	−0.2074 (8)	3.0 (3)
C18	0.6288 (6)	1.0914 (6)	−0.101 (1)	3.0 (3)
C19	0.6722 (5)	1.0916 (5)	0.0741 (8)	2.6 (3)
C20	0.6973 (7)	1.1864 (6)	0.192 (1)	3.4 (3)
C21	0.7344 (8)	1.1785 (6)	0.355 (1)	4.0 (3)
C22	0.7509 (7)	1.0753 (6)	0.4041 (9)	3.4 (3)
C23	0.6885 (5)	0.9907 (5)	0.1327 (7)	2.1 (2)
C24	0.6613 (5)	0.8901 (5)	0.0197 (7)	2.1 (2)

[a] $B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\cdot\mathbf{a}_j$.

either would not refine or did not significantly lower the R factor. A Fourier difference map eventually revealed that the Tc was also disordered. Only when Tc* was correctly placed with its B value constrained to that of the original Tc and isotropically refined, first upon population and then upon position, could Cl*, and finally N1*, be sequentially introduced in a similar fashion upon subsequent series of refinement cycles. Disorder in the hexafluorophosphates was then treated by locating the disordered atoms and refining on all the P and F atoms alone with respect to position and population. The population of the fluorides was then fixed at 0.5, and the P and F atoms were refined anisotropically. In the final refinement, all atoms were refined anisotropically, except Tc*, Cl*, and N1*, which were held isotropic at fixed B values and populations (15%). Atomic positions are listed in Table III.

Calculations. ZINDO[15] and molecular mechanics (MM2)[16] calculations were performed on a CaChe workstation[17] by using the crystallographic coordinates in Tables II and III.

Results

Compound Characterization. Slight differences in the physical properties of the chloride and hexafluorophosphate salts in the solid state are indicated in the Experimental Section. In both compounds, two Tc≡N stretching frequencies appeared, which were consistently 3–8 cm^{-1} higher in energy for the chloride relative to the hexafluorophosphate salt, while most other bands were within experimental error (±1 cm^{-1}). HPLC of one batch of [NCl(phen)$_2$Tc]PF$_6$, on which a structure determination had been performed and which was identical in its solution properties to [NCl(phen)$_2$Tc]Cl, showed only a single peak. Because of their low symmetry and slight paramagnetism, the ^{99}Tc NMR spectra of I and II in DMF-d_7 were extremely broad (line widths of ~8000 Hz) and centered at 6150 ppm relative to [^{99}TcO$_4$]$^-$.[18]

In CD$_3$CN, the ^{1}H NMR spectra of the two salts were significantly different; however, both were dependent on water content and their spectral differences are attributed to different water concentrations. When this variable was removed by combining the two solutions, only the ^{1}H NMR spectrum of the chloride salt was observed. Unambiguous differences were observed in two preparations of the hexafluorphosphate salt relative to the chloride in DMF-d_7, where the ^{1}H NMR spectra of the two isomers are distinguishable both in separate solutions and in combination (see supplementary Figure 1s). Evidence of significant impurities is absent from these NMR spectra, and COSY analysis revealed that all peaks could be attributed to phenanthroline ligands. When the compound was heated to 80 °C in DMF, the spectrum of the hexafluorphosphate salt disappeared and only that of the chloride salt remained at this or lower temperatures, suggesting that a kinetic stability may sometimes be conferred on II in this solvent. Consistent with the observation of NMR signals, ESR spectra were not observed.

Both compounds give irreversible cyclic voltammetric reduction waves in 0.1 M TEAP in DMF at −1.04 ± 0.04 V (vs NHE). However, two batches of the hexafluorophosphate salt exhibited this wave at −0.9 V and the difference of ~0.1 V between these

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(15) Anderson, W. P.; Cundarai, T. R.; Drago, R. S.; Zerner, M. C. *Inorg. Chem.* **1990**, *29*, 1.

(16) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(17) Version 2.7, CAChe Scientific, Inc., Beaverton, OR, 1991.

(18) O'Connell, L.; Pearlstein, R.; Davison, D.; Thornback, J.; Kronauge, J.; Jones, A. *Inorg. Chim. Acta* **1989**, *161*, 39.

Table III. Crystallographic Coordinates, Populations, and Isotropic Thermal Parameters for Atoms in $[NCl(phen)_2Tc]PF_6$

atom	*x*	*y*	*z*	pop.	*B*,[a] Å^2
Tc	0.82219 (4)	0.35511 (4)	0.24559 (3)	0.85	2.65 (1)
Tc*	0.8211 (3)	0.3614 (3)	0.2135 (2)	0.15	2.7
Cl	0.9326 (1)	0.3476 (2)	0.1541 (1)	0.85	4.13 (7)
Cl*	0.864 (1)	0.234 (1)	0.339 (1)	0.15	4.2
N1	0.8702 (6)	0.2584 (5)	0.3184 (4)	0.85	4.4 (3)
N1*	0.911 (3)	0.336 (4)	0.170 (3)	0.15	4.5
N2	0.7090 (3)	0.2619 (3)	0.1320 (3)	1.0	3.1 (1)
N3	0.7212 (3)	0.4747 (3)	0.1188 (3)	1.0	2.9 (1)
N4	0.7177 (3)	0.4118 (3)	0.3094 (3)	1.0	3.2 (2)
N5	0.9067 (3)	0.4872 (3)	0.3263 (3)	1.0	2.8 (1)
C1	0.7001 (4)	0.1564 (4)	0.1377 (4)	1.0	3.9 (2)
C2	0.6325 (5)	0.0953 (4)	0.0623 (4)	1.0	4.3 (2)
C3	0.5728 (4)	0.1421 (5)	−0.0231 (4)	1.0	4.5 (2)
C4	0.5776 (4)	0.2528 (4)	−0.0340 (4)	1.0	3.5 (2)
C5	0.5177 (4)	0.3074 (5)	−0.1208 (4)	1.0	4.4 (2)
C6	0.5259 (4)	0.4132 (5)	−0.1268 (4)	1.0	4.4 (2)
C7	0.5947 (4)	0.4735 (4)	−0.0474 (3)	1.0	3.3 (2)
C8	0.6048 (4)	0.5856 (4)	−0.0491 (4)	1.0	4.1 (2)
C9	0.6707 (5)	0.6373 (4)	0.0301 (4)	1.0	4.1 (2)
C10	0.7288 (4)	0.5796 (4)	0.1138 (4)	1.0	3.6 (2)
C11	0.6554 (4)	0.4233 (4)	0.0395 (3)	1.0	3.1 (2)
C12	0.6472 (4)	0.3098 (4)	0.0453 (3)	1.0	3.0 (2)
C13	0.6260 (4)	0.3722 (4)	0.3006 (4)	1.0	4.4 (2)
C14	0.5691 (4)	0.4129 (5)	0.3507 (5)	1.0	5.0 (3)
C15	0.6091 (5)	0.4946 (5)	0.4155 (4)	1.0	4.7 (3)
C16	0.7074 (4)	0.5356 (4)	0.4289 (4)	1.0	3.8 (2)
C17	0.7568 (5)	0.6185 (5)	0.4940 (4)	1.0	4.9 (3)
C18	0.8512 (5)	0.6575 (4)	0.5026 (4)	1.0	4.7 (2)
C19	0.9047 (4)	0.6174 (4)	0.4457 (4)	1.0	3.4 (2)
C20	1.0021 (5)	0.6548 (4)	0.4483 (4)	1.0	4.2 (2)
C21	1.0479 (4)	0.6094 (4)	0.3915 (4)	1.0	4.0 (2)
C22	0.9988 (4)	0.5251 (4)	0.3314 (4)	1.0	3.5 (2)
C23	0.8596 (4)	0.5330 (4)	0.3815 (3)	1.0	2.9 (2)
C24	0.7588 (4)	0.4922 (4)	0.3730 (3)	1.0	3.0 (2)
P	1.2848 (1)	0.6270 (1)	0.2802 (1)	1.0	4.20 (6)
F1	1.2242 (9)	0.723 (1)	0.304 (1)	0.5	8.5 (5)
F2	1.218 (1)	0.537 (1)	0.305 (1)	0.5	10.7 (6)
F3	1.361 (1)	0.625 (1)	0.392 (1)	0.5	8.9 (6)
F4	1.208 (1)	0.638 (1)	0.1703 (8)	0.5	9.7 (5)
F5	1.3538 (8)	0.7155 (7)	0.2629 (8)	0.5	6.3 (4)
F6	1.3434 (7)	0.5351 (8)	0.2491 (8)	0.5	5.5 (4)
F1*	1.1811 (8)	0.566 (1)	0.2536 (8)	0.5	8.6 (5)
F2*	1.308 (2)	0.622 (2)	0.390 (1)	0.5	13 (1)
F3*	1.226 (1)	0.730 (1)	0.279 (1)	0.5	12.7 (8)
F4*	1.345 (1)	0.525 (1)	0.279 (1)	0.5	17 (1)
F5*	1.258 (1)	0.629 (2)	0.172 (1)	0.5	14 (1)
F6*	1.391 (1)	0.683 (1)	0.301 (1)	0.5	14.1 (9)

[a] $B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table IV. Comparison of Theoretical and Experimental Bond Lengths around the Technetium in I and II

bond	opt[a] distance, Å	I distance, Å	II distance, Å
Tc–N1	1.627 (1)	1.603 (5)	1.593 (5)
Tc–N2	2.187 (1)	2.135 (5)	2.153 (4)
Tc–N3	2.288 (4)	2.399 (5)	2.395 (4)
Tc–N4	2.199 (2)	2.123 (5)	2.133 (4)
Tc–N5	2.184 (1)	2.122 (5)	2.118 (4)
Tc–Cl	2.553 (1)	2.412 (2)	2.405 (2)
Tc–*xy* plane[b]		0.362 (1)	0.334 (4)

[a] Average of ZINDO (INDO/1) geometry optimizations starting from I and II. [b] *xy* plane is defined by N2, N4, N5, and Cl.

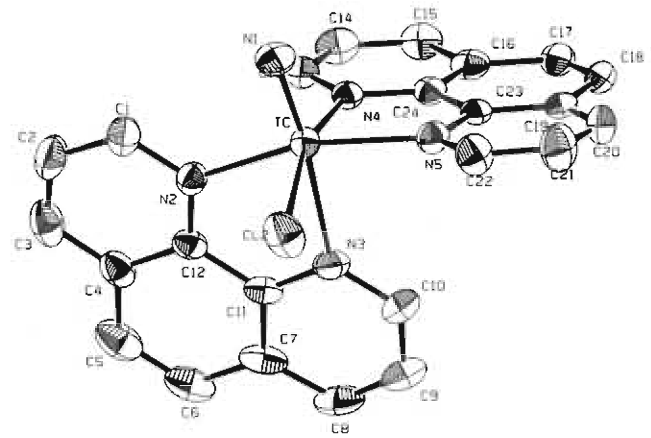

Figure 1. ORTEP[33] diagram of $[NCl(phen)_2Tc]^+$ from the crystal of $[NCl(phen)_2Tc]Cl{\cdot}H_2O$. Aromatic hydrogens have been removed for clarity. Thermal ellipsoids are at 50% probability.

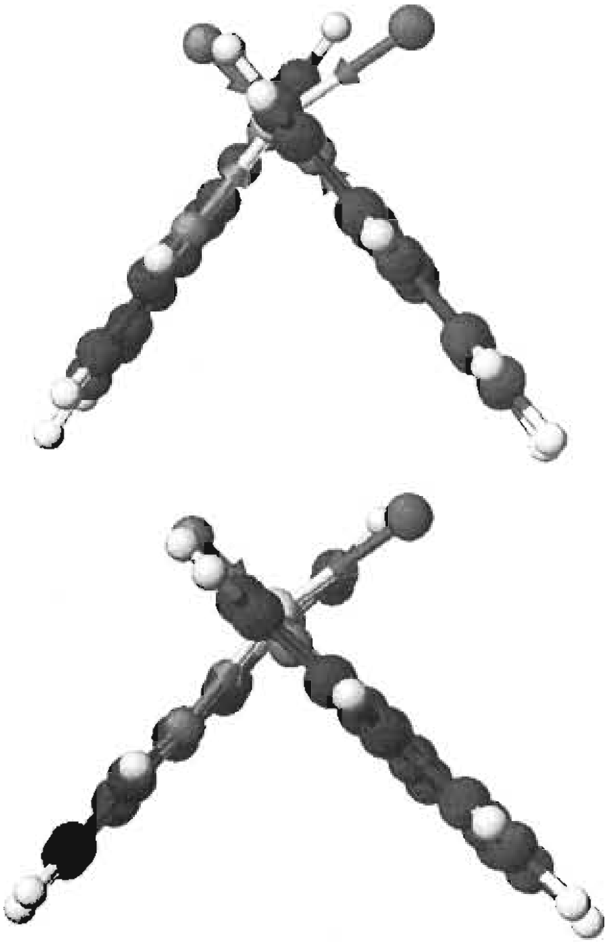

Figure 2. CaChe Molecular Editor drawing of (a, top) I and (b, bottom) II, which were made by using the atomic coordinates in Tables II and III, respectively.[17]

waves of the two salts was evident even in the same solution (see supplementary Figure 2s). Consistent with the nature of the lowest LUMO's (see below), these waves are attributed to reduction of the phenanthroline ligand and are similar to that seen for *cis*-$[N(CF_3CO_2)(phen)_2Tc]^+$ (−1.03 V) in DMF.[19]

Structure of *cis*-$[NCl(phen)_2Tc]^+$. The structure of the complex ion from $[NCl(phen)_2Tc]Cl{\cdot}H_2O$ is shown in Figure 1 and that from $[NCl(phen)_2Tc]PF_6$ is given in Figure 3s. The bond distances and angles surrounding the essentially octahedral technetium atoms are compared in Tables IV and V, respectively. The dihedral angles between phen1 (containing N2 and N3) and phen2 (containing N4 and N5) in the two structures are 73.85 and 89.23° for the chloride and hexafluorophosphate salts, respectively. The dihedral angle between phen1 and the plane defined by N1, N2, N3, and N5 is 5.7° in I and −5.3° in II, which places C1–H1 on opposite sides of N1 between the two structures, as shown in Figure 2.

In the crystal packing of $[NCl(phen)_2Tc]Cl{\cdot}H_2O$ there is substantial (43%) overlap of symmetry-related phen2's with a mean separation of 3.44 (4) Å. Phen1 overlaps (21%) with the

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(19) Lu, J. Ph.D. Thesis, Boston College, 1991.

Table V. Bond Angles Surrounding the Tc Atom in [NCl(phen)$_2$Tc]Cl·H$_2$O and [NCl(phen)$_2$Tc]PF$_6$

	[NCl(phen)$_2$Tc]Cl· H$_2$O		[NCl(phen)$_2$Tc]PF$_6$	
bond	angle, deg	σ_1	angle, deg	σ_2
N1–Tc–N2	98.0	0.2	95.9	0.3
N1–Tc–N3	170.0	0.2	168.0	0.3
N1–Tc–N4	97.7	0.2	97.3	0.3
N1–Tc–N5	101.3	0.3	102.8	0.3
N1–Tc–Cl	100.9	0.2	99.6	0.3
N2–Tc–N3	73.2	0.3	72.5	0.1
N2–Tc–N4	92.0	0.2	97.0	0.2
N2–Tc–N5	159.4	0.2	161.3	0.2
N2–Tc–Cl	90.5	0.1	87.7	0.1
N3–Tc–N4	78.3	0.2	81.5	0.1
N3–Tc–N5	86.9	0.2	88.8	0.2
N3–Tc–Cl	84.1	0.1	83.2	0.2
N4–Tc–N5	78.3	0.2	78.7	0.2
N4–Tc–Cl	160.6	0.1	161.9	0.1
N5–Tc–Cl	92.9	0.1	91.2	0.1

phen1 of an inversion-related enantiomer and secondarily (14%) with phen1 on a second enantiomer at 3.39 (3) Å. The two chlorides lie between the two inversion-related complexes in the unit cell and are each hydrogen bonded to separate water molecules. In [NCl(phen)$_2$Tc]PF$_6$, the packing is somewhat less dominated by stacking of the *o*-phenanthroline rings, with the edge of phen2 stacking with a symmetry-related phen2 to give a 29% overlap at an interplane distance of 3.43 (1) Å. phen1 has overlapping interactions with two separate, symmetry-related phen1's, with the extent of overlap to each being about 21% and a closest contact between C9's (3.38 Å) and an average distance of 3.47 (8) Å for the three-atom edge. The approach of phen1 to a 2_1-symmetry related phen1 is at a slight (13°) angle. The volume available for the complex itself, $(V_{\mathrm{cell}} - zV_{\mathrm{anion}})/z$, is about 535 Å^3 for the two structures, and the closest symmetry-related technetium centers in the structures are at similar distances (7.400 (2) Å). In the chloride salt, the water molecule and ionic chloride form an oblong shape that the complex ion must pack around, while in the hexafluorophosphate salt the counterion is both larger and more symmetrical and the ions are related by a 2_1 screw axis.

Calculations. ZINDO calculations on ions I and II indicated that I is 3.6 kcal lower in energy than II in the gas phase. Comparisons of the core repulsion energies and molecular mechanics energies revealed that II has somewhat less steric repulsion than I. The sums of the Wyberg bond indices involving the Tc are essentially identical in I (6.15) and II (6.14). The potential energy well produced by varying only the Tc$\equiv$N bond length was fit to the equation $V = C_e + k(R - R_e)^2$, with R_e = 1.6457 (7) Å, k = 1081 (6) kcal/Å^2. Similar calculations on the Tc—Cl bond gave R_e = 2.609 (3) Å, k = 156.1 (9) kcal/Å^2. Analogous calculations involving rotation of phen1 to vary the phen1—phen2 dihedral angle gave somewhat dissimilar curves with minimum energy angles of 84.5 and 93.2° and k values of 0.0112 and 0.0136 kcal/deg^2 for I and II. The two highest HOMO's in either structure are essentially antibonding combinations of d_{xy} and chloride p_x orbitals along with some nonbonding π-orbitals on phen1, while the two lowest LUMO's are nonbonding π-orbitals on phen2. Energy optimization of either structure yielded essentially the same structure with the bond lengths listed in Table IV.

Discussion

The Tc$\equiv$N distances (average = 1.598 Å) reported here are similar to those found in [N(CF$_3$CO$_2$)(phen)$_2$Tc](CF$_3$CO$_2$)·H$_2$O (average = 1.60$_5$ Å)[19] and comparable with the average Tc$\equiv$N bond lengths (1.616 (8) Å) of a number of other Tc$^{\mathrm{V}}$—nitrido complexes.[20-29] By using the parabolic fit parameter for this bond, it can be estimated that the 0.8 kcal/mol needed to compress the Tc$\equiv$N distance from the idealized distance given by ZINDO calculations to the experimentally observed values (cf. Table IV) could easily be introduced by packing forces. The equatorial and axial Tc—N bond distances in the present structures are within the range expected from the average derived from previous work (2.11 (3) and 2.45 (5) Å, respectively).[20,22,25,30] The equatorial Tc—Cl distances are significantly shorter than that in the ZINDO-optimized geometry (Table IV) and the most directly comparable value of 2.441 Å found in [NCl$_2$(PMe$_2$Ph)$_3$Tc$^{\mathrm{V}}$];[26] however, they are within the range of the average of several other Tc$^{\mathrm{V}}$—Cl bond distances (2.36 (7) Å)[30] and the parabolic k value for this bond leads to the estimation that only 3.3 kcal/mol would need to be provided by packing forces to compress this bond from the idealized to the experimental value. The small values of μ_{eff} are probably due to temperature-independent paramagnetism, which is common in tetragonally distorted d^2 ions.

ZINDO calculations suggest that I and II are of similar energies, with I having greater electronic stability and II having less steric repulsion. While the bond lengths in I and II are virtually identical (cf. Table IV), the adaptation of the complex to the two different symmetry environments of their packing sites causes II to be the more symmetric and to exhibit less stacking of its *o*-phenanthroline rings. The resulting near-2-fold symmetry of II bisecting the N1–Tc–Cl angle, which is clearly evident in Figure 2b, gives rise to the enantiomeric disorder present in the hexafluorophosphate salt. The different minima yielded by I and II in their dihedral angle potential wells, which correctly placed the C1–H on different sides of N1, suggest a barrier to this rotation that could give rise to "twistomers" and account for their occasional ^{1}H NMR differences in DMF, which disappear on heating. However, a two-dimensional molecular mechanics search of the energy surface defined by the phen1–N1 and phen2–Cl dihedral angles revealed no significant barrier.

In CD$_3$CN, ^{1}H NMR differences in the spectra of I and II are due to variations in water concentrations, which may arise from protonatation or hydrogen bonding to the nucleophilic nitrido ligand and concomittant modulation of the Tc$\equiv$N bond. The lower reduction potential evident in two samples of *cis*-[NCl(phen)$_2$Tc](PF$_6$) in DMF (cf. $E°$'s in Results) is difficult to explain in terms of a phenanthroline ligand reduction, since ZINDO calculations yielded phen2-centered LUMO's for I (−0.601 eV) and II (−0.430 eV) such that the reduction of this ligand should be *more* difficult in II than in I.

Conclusion. Distortions generated by packing forces can give rise to pseudosymmetry in some complexes, resulting in enantiomeric disorder, which can lead to *reproducible* bond length errors in a *pure* compound that correlate well with those predicted for "bond stretch" isomers. The low k value for varying the phen1–phen2 dihedral angle suggests that complexes with phenanthroline-like ligands employed for shape recognition in nucleic acid structures[31,32] could be easily distorted upon binding to the biopolymer, so that the shapes evident in the crystal structures of these molecules may be significantly different from those of

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(20) Baldas, J.; Bonnyman, J.; Pojer, P. M.; G. A., W. *J. Chem. Soc., Dalton Trans.* **1981**, 1798–1801.

(21) Baldas, J.; Bonnyman, J.; Williams, G. A. *Inorg. Chem.* **1986**, *25*, 150—153.

(22) Baldas, J.; Bonnyman, J.; Williams, G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 833–837.

(23) Marchi, A.; Duatti, A.; Rossi, R.; Magnon, L.; Pasqualine, R.; Bertolasi, V.; Feretti, V.; Gilli, G. *J. Chem. Soc., Dalton Trans.* **1988**, 1743–1749.

(24) Colmanet, S. F.; Mackay, M. F. *Inorg. Chim. Acta* **1988**, *147*, 173–178.

(25) de Vries, N.; Costello, C. E.; Jones, A. G.; Davison, A. *Inorg. Chem.* **1990**, *29*, 1348–1352.

(26) Batsanov, A. S.; Struchkov, Y. T.; Lorenz, B.; Olk, B. *Z. Anorg. Allg. Chem.* **1988**, *564*, 129–134.

(27) Marchi, A.; Rossi, R.; Magon, L.; Duatti, A.; Casellato, U.; Graziani, R.; Vital, M.; Riche, F. *J. Chem. Soc., Dalton Trans.* **1990**, 1935–1940.

(28) Archer, C. M.; Dilworth, J. R.; Kelly, J.; Duncan, M.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1989**, 375–376.

(29) Duatti, A.; Marchi, A.; Bertolasi, V.; Ferretti, V. *J. Am. Chem. Soc.* **1991**, *113*, 9680–9682.

(30) Bandoli, G.; Mazzi, U.; Roncari, E.; Deutsch, E. *Coord. Chem. Rev.* **1982**, *44*, 191–227.

(31) Pyle, A. M.; Barton, J. K. In *Bioinorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1990; Vol. 38, pp 413–474.

(32) Chow, C. S.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 2839–2841.

the recognition species. Distortions such as the one noted here, which generate a pseudo-2-fold rotation axis, may arise in binding to DNA dyad structures.

Acknowledgment. We gratefully acknowledge Dr. Sam Cole (CAChe Group) for helpful suggestions regarding electronic and molecular mechanics calculations; Dr. Lynne A. O'Connell for obtaining the ^{99}Tc NMR spectra; Prof. Marj Kastner (Bucknell) for initially suggesting enantiomeric disorder and Prof. Bruce Foxman (Brandeis) and a referee for reinforcing this suggestion; and Prof. Martha Teeter for providing X-ray and computer facilities, which were funded by Boston College and NSF Grant BBS-8617930. Experimental work was supported by NSF Grant CHE-8618011, and final data analysis, by NIH Grant GM-26390.

Supplementary Material Available: Figures showing ^{1}H NMR spectra and square-wave voltammetric scans of *cis*-[NCl(phen)$_2$Tc]Cl·H$_2$O and [NCl(phen)$_2$Tc]PF$_6$ in DMF, square-wave voltammetric scans of *cis*-[NCl(phen)$_2$Tc]$^+$ in DMF, an ORTEP diagram of [NCl(phen)$_2$Tc]PF$_6$, and infrared spectra and tables of complete crystallographic data, temperature factors for non-hydrogen atoms, complete bond distances and angles, and results of calculations of least squares planes (29 pages); listings of calculated and observed structure factor amplitudes (42 pages). Ordering information is given on any current masthead page.[33-37]

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(33) Johnson, C. K. ORTEPII. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(34) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(35) Cromer, D. T.; Weber, J. T. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV; Tables 2.2 A and 2.3.1.

(36) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42–46.

(37) Beurskens, P. T. DIRDIF. Technical Report; University of Nijmegen, Crystallographic Laboratory: Nijmegen, The Netherlands 1984.

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New 12-Membered and 24-Membered Macrocycles with Pendent Acetato Groups and X-ray Crystal Structures of the Copper(II) and Manganese(II) Complexes

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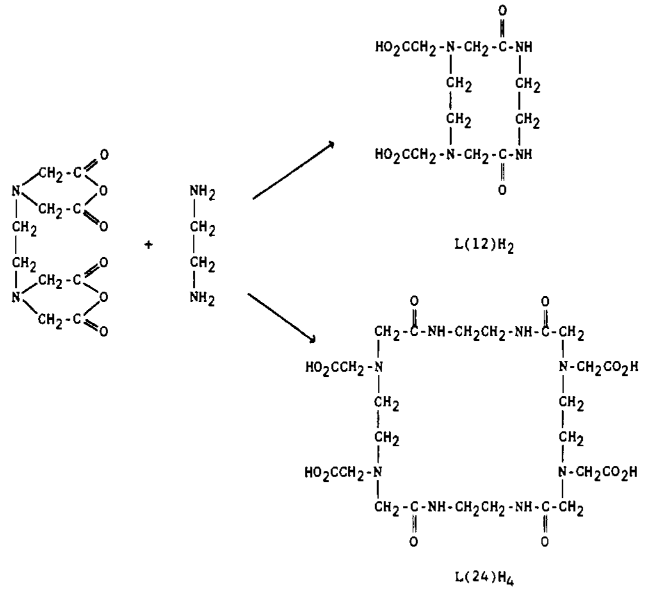
Received October 4, 1991

A condensation reaction between ethylenediaminetetraacetic dianhydride and ethylenediamine provided two new macrocyclic ligands: one is a 12-membered macrocycle with two pendent acetato groups, $C_8H_{14}N_4O_2(CH_2CO_2H)_2$ [represented as L(12)H$_2$], and the other is a 24-membered macrocycle with four pendent acetato groups, $C_{16}H_{28}N_8O_4(CH_2CO_2H)_4$ [represented as L(24)H$_4$], in which two ethylenediaminetetraacetato groups and two ethylenediamine groups are linked by amide bonds. The formation of the macrocycles was confirmed by X-ray crystal analyses of their metal complexes, CuL(12)·4H$_2$O and Mn$_2$L(24)·8H$_2$O. The copper(II) complex crystallized in the orthorhombic space group $P2_12_12_1$ with a = 10.070 (1) Å, b = 18.832 (2) Å, c = 9.425 (1) Å, and Z = 4. Each copper atom has a distorted octahedral coordination geometry with two amine nitrogen atoms (Cu–N = 2.088 and 2.485 Å), an amide oxygen atom (Cu–O = 1.988 Å), two carboxylato oxygen atoms (Cu–O = 1.996 and 2.334 Å), and another carboxylato oxygen atom from a neighboring metal chelate (Cu–O = 1.936 Å); one of the amide groups is not coordinated to copper. One of the carboxylato groups is coordinated to two copper atoms, forming a one-dimensional –Cu–O–C–O–Cu– chain. The manganese complex crystallized in the hexagonal space group $P6_2$ (or $P6_4$) with a = 18.072 (3) Å, c = 10.195 (2) Å, and Z = 3. Each ligand coordinates two manganese ions, which are located outside the cavity of the macrocycle and are crystallographically equivalent to each other. Each manganese atom has a distorted seven-coordination geometry with two amine nitrogen atoms (Mn–N = 2.358 and 2.445 Å), two carboxylato oxygen atoms (Mn–O = 2.111 and 2.212 Å), a water molecule (Mn–O = 2.137 Å), and two amide oxygen atoms (Mn–O = 2.184 and 2.686 Å).

Introduction

The coordination chemistry of macrocyclic multidentate ligands is an established and important field.[2-4] Recently, a great deal of interest has been directed to metal complexes with functionalized macrocycles that have pendent functional groups such as amine, hydroxy, and carboxylato groups.[4-9] In attempts to synthesize new aliphatic macrocycles with pendent acetato groups, we have carried out a condensation reaction with ethylenediaminetetraacetic dianhydride and ethylenediamine. This reaction has resulted in the formation of two macrocycles as shown in Scheme I. One [represented as L(12)H$_2$] is a 12-membered macrocycle that has two pendent acetato groups, and the other [represented as L(24)H$_4$] is a 24-membered macrocycle with four pendent acetato groups. The formation of the macrocyclic rings

Scheme I



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(1) (a) University of Arizona. (b) Universidad de Sonora. (c) On leave from Cosmo Oil Co., Tokyo, Japan, under a contract with the Japan International Cooperation Agency.

(2) Izatt, R. M., Christensen, J. J., Eds. *Synthetic Multidentate Macrocyclic Compounds*; Academic Press: New York, 1978.

(3) Melson, G. A. *Coordination Chemistry of Macrocyclic Compounds*; Plenum Press: New York, 1979.

(4) Bernhardt, P. V.; Lawrance, G. A. *Coord. Chem. Rev.* **1990**, *104*, 297.

(5) Parker, D. *Chem. Br.* **1990**, 942.

(6) Moore, D. A.; Fanwick, P. E.; Welch, M. J. *Inorg. Chem.* **1990**, *29*, 672.

(7) Clark, P.; Lincoln, S. F.; Wainwright, K. P. *Inorg. Chem.* **1991**, *30*, 174.

(8) Brucher, E.; Cortes, S.; Chavez, F.; Sherry, A. D. *Inorg. Chem.* **1991**, *30*, 2092.

(9) Perkovic, M. W.; Heeg, M. J.; Endicott, J. F. *Inorg. Chem.* **1991**, *30*, 3140.

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