Table II. Final Positional and Thermal Parameters for $Ph_4As[TcO(SCH_2CH_2O)_2]$[a]

atom	*x*	*y*	*z*	*U*(1,1)	*U*(2,2)	*U*(3,3)	*U*(1,2)	*U*(1,3)	*U*(2,3)
Tc	0.560 15 (5)	0.466 46 (4)	0.292 63 (4)	0.0477 (4)	0.0351 (4)	0.0467 (4)	0.0003 (4)	−0.0055 (4)	−0.0113 (4)
As	0.400 86 (5)	0.165 75 (4)	0.457 28 (4)	0.0340 (4)	0.0327 (4)	0.0305 (4)	−0.0003 (4)	−0.0007 (4)	−0.0002 (4)
S_1	0.701 3 (2)	0.427 0 (1)	0.314 3 (1)	0.054 (1)	0.059 (1)	0.058 (1)	0.010 (1)	−0.000 (1)	−0.002 (1)
S_2	0.522 3 (2)	0.411 6 (2)	0.395 8 (2)	0.081 (2)	0.071 (2)	0.101 (2)	0.022 (2)	0.035 (2)	0.037 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
O_1	0.6208 (4)	0.5521 (3)	0.2555 (3)	4.5 (1)	C_{14}	0.3154 (7)	−0.0748 (5)	0.4857 (5)	4.7 (2)
O_2	0.4808 (4)	0.5417 (3)	0.3249 (3)	4.3 (1)	C_{15}	0.2771 (7)	−0.0230 (5)	0.5261 (5)	5.2 (2)
O_3	0.5171 (5)	0.4201 (4)	0.2266 (4)	6.3 (2)	C_{16}	0.3044 (6)	0.0512 (5)	0.5198 (5)	4.0 (2)
C_1	0.7111 (8)	0.5443 (6)	0.2335 (6)	6.7 (3)	C_{17}	0.5082 (5)	0.1783 (4)	0.4066 (4)	2.8 (2)
C_2	0.7692 (9)	0.4989 (7)	0.2739 (7)	7.9 (3)	C_{18}	0.5755 (6)	0.2197 (5)	0.4351 (5)	3.7 (2)
C_3	0.4275 (7)	0.5349 (6)	0.3866 (6)	5.6 (2)	C_{19}	0.6530 (6)	0.2327 (5)	0.3949 (5)	4.5 (2)
C_4	0.4154 (8)	0.4586 (7)	0.4072 (6)	6.8 (3)	C_{20}	0.6604 (7)	0.2014 (5)	0.3293 (5)	4.7 (2)
C_5	0.3086 (5)	0.2122 (4)	0.4047 (4)	2.6 (2)	C_{21}	0.5929 (6)	0.1607 (5)	0.3017 (5)	4.3 (2)
C_6	0.2203 (6)	0.1923 (4)	0.4152 (4)	3.5 (2)	C_{22}	0.5144 (6)	0.1478 (4)	0.3398 (4)	3.1 (2)
C_7	0.1524 (6)	0.2281 (5)	0.3791 (5)	4.5 (2)	C_{23}	0.4058 (5)	0.2160 (4)	0.5446 (4)	2.7 (2)
C_8	0.1757 (6)	0.2830 (5)	0.3320 (5)	4.4 (2)	C_{24}	0.3966 (6)	0.2909 (5)	0.5417 (4)	3.6 (2)
C_9	0.2650 (6)	0.3023 (5)	0.3208 (5)	4.4 (2)	C_{25}	0.3987 (6)	0.3297 (5)	0.6046 (5)	4.0 (2)
C_{10}	0.3335 (6)	0.2666 (5)	0.3584 (4)	3.6 (2)	C_{26}	0.4110 (6)	0.2948 (5)	0.6668 (5)	4.3 (2)
C_{11}	0.3706 (5)	0.0667 (4)	0.4716 (4)	2.8 (2)	C_{27}	0.4208 (6)	0.2199 (5)	0.6682 (5)	4.0 (2)
C_{12}	0.4130 (6)	0.0138 (5)	0.4301 (5)	3.7 (2)	C_{28}	0.4180 (5)	0.1798 (4)	0.6066 (4)	3.1 (2)
C_{13}	0.3829 (7)	−0.0587 (5)	0.4386 (5)	4.9 (2)					

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta(1,1)^*h^2 + \beta(2,2)^*k^2 + \beta(3,3)^*l^2 + \beta(1,2)^*hk + \beta(1,3)^*hl + \beta(2,3)^*kl)]$.

Table III. Selected Distances (Å) and Selected Angles (Deg)

atom	atom	dist	atom	atom	dist
Tc	S_1	2.283 (2)	S_2	C_4	1.841 (9)
Tc	S_2	2.297 (2)	O_1	C_1	1.429 (9)
Tc	O_1	1.963 (4)	O_2	C_3	1.435 (9)
Tc	O_2	1.936 (4)	C_1	C_2	1.438 (11)
Tc	O_3	1.662 (5)	C_3	C_4	1.478 (11)
S_1	C_2	1.848 (10)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
S_1	Tc	S_2	86.09 (7)	O_2	Tc	O_3	112.0 (2)
S_1	Tc	O_1	83.8 (1)	Tc	S_1	C_2	101.9 (3)
S_1	Tc	O_2	138.1 (1)	Tc	S_2	C_4	96.3 (3)
S_1	Tc	O_3	109.7 (2)	Tc	O_1	C_1	117.9 (4)
S_2	Tc	O_1	141.8 (2)	Tc	O_2	C_3	123.0 (4)
S_2	Tc	O_2	83.6 (1)	O_1	C_1	C_2	118.5 (8)
S_2	Tc	O_3	109.4 (2)	S_1	C_2	C_1	108.2 (7)
O_1	Tc	O_2	79.8 (2)	O_2	C_3	C_4	112.0 (6)
O_1	Tc	O_3	108.7 (2)	S_2	C_4	C_3	108.2 (6)

Å) or **3** (0.791 (3) Å). It has been proposed[10] that the steric demands of the oxo—oxygen in dichloro[hydrotris(1-pyrazolyl)borato]oxotechnetium(V) (**4**) cause the cis ligands to bend away from the Tc=O moiety in the compound. If such an explanation were invoked to explain the relatively short metal-to-basal plane distance in **1**, it might be expected that the O_3-Tc-$O_{1,2}$(av) angle would be significantly smaller than the O_3-Tc-$S_{1,2}$(av) angle. This is not so. The average angles are 110.4 (2) and 109.6 (2)°, respectively. Indeed, O_3-Tc-O_2 is the largest angle of the set. The average O-Tc-S angle in the $TcOS_4$ core of **3** is 110.0 (3)°, and in **2** it is 109.3 (4)°. It can be concluded that the short Tc-to-basal plane distance in **1** is entirely due to the relative Tc-S and Tc-O(ligand) bond lengths and not to sterically induced bond angle deformation.

Although the cis form of **1** was isolated, there is no a priori reason to doubt the existence of the trans isomer. A similar situation occurred for **3**; the cis isomer was isolated, but the trans isomer could be detected by NMR in the unfractionated reaction product. Complex **1** has a moderately intense band in its optical spectrum (λ_{max}(MeCN) = 357 nm; ϵ = 2770 L mol^{-1} cm^{-1}) and a much weaker one (λ_{max} = 525 nm, ϵ = 180 L mol^{-1} cm^{-1}). Any bands at shorter wavelengths are obscured by the absorptions of the tetraphenylarsonium ion. The more intense band has position and extinction coefficient similar to the principle features in the spectra of **2** and **3** and is most likely due to sulfur-to-metal charge-transfer absorption. The weaker band by virtue of its position and intensity may be a d-d transition. The infrared spectrum of **1** (KBr pellet) exhibits a strong band at 948 cm^{-1}, with a weaker, poorly resolved shoulder at 935 cm^{-1} which can be attributed to the technetium-oxo stretching mode (the splitting probably results from a solid-state effect).

The isolation of **1** demonstrates the ease with which the oxotechnetium(V) core is formed during the aerobic reduction of pertechnetate and that the TcO^{3+} core can be stabilized by donors other than four bischelated sulfur atoms. This enlarges the scope of potential ligands for rationally designed radiopharmaceuticals.

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Registry No. 1, 76584-36-6.

Supplementary Material Available: A table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Adiabatic Potential Surface of the Hexafluorocupric Ion: Contribution to the Stereochemistry of Copper(II) Complexes

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The statistical analysis of X-ray structural data for Cu(II) complexes with certain chromophores, stimulated largely by the earlier works of Hathaway and co-workers,[1-3] yields some

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Chart I

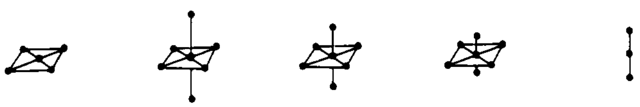

Table I. Experimental Values of R_a and R_e for the CuF_6 Chromophore

no.	compd	coord no.[a]	type of unit[a]	R_a	R_e	method[b]	ref
1	Na_2CuF_4	4 + 2	B	2.37	1.91	X	10
2	Ba_2CuF_6	4 + 2	B	2.33	1.89	N	11
2	Ba_2CuF_6	4 + 2	B	2.32	1.87	X	12
3	K_2CuF_4	4 + 2	B	2.28	1.91	X	13
4	$CuF_2(s)$	4 + 2	B	2.27	1.93	X	14
5	$NaCuF_3$	4 + 2	B	2.26	1.93	X	15
6	$KCuF_3$	4 + 2	B	2.26	1.92	N	16
6	$KCuF_3$	4 + 2	B	2.25	1.93	X	17
3	K_2CuF_4	4 + 2	B	2.22	1.92	X	18
6	$KCuF_3$	2 + 4	D	1.96	2.07	X	19
3	K_2CuF_4	2 + 4	D	1.95	2.08	X	20
2	Ba_2CuF_6	2 + 4	D	1.85	2.08	E	21
7	$CuF_2(g)$	2	E	1.72		E	22

[a] According to Chart I. [b] Key: X, X-ray structural analysis; N, neutron diffraction; E, estimate.

new concepts in modern stereochemistry.[4-9] The well-known tetragonal distortions of coordination polyhedra with CuN_6, CuO_6, and CuN_4O_2 chromophores exhibit interesting correlations between the variation of the axial, R_a, and the equatorial, R_e, interatomic distances for the coordination number of 4 + 2.[4-6] Originally, the former distance was marked as R_L (long), while the latter was marked R_S (short) because the distortions toward the elongated tetragonal bipyramid appear to be typical for coordination polyhedra of Cu(II).[4] The above-mentioned correlations are manifested in the fact that with increasing R_a the distance R_e decreases and vice versa. In the large statistical set of X-ray data the R_a vs. R_e dependence becomes practically continuous. This is the case of the CuO_6 chromophore (73 experimental points[4]) where distances Cu–O cover the range of values $R_e \in \langle 1.88, 2.15 \rangle$ and $R_a \in \langle 1.97, 3.50 \rangle$ (all distances in 10^{-10} m). The lower limit of $R_e^{\min} \approx 1.9$ corresponds to the upper limit of $R_a^{\max} \approx 3.5$ where the chemical interactions may be ruled out and the complex becomes rather a square-planar one. A pair of experimentally determined internal coordinates $\{R_a,R_e\}$ corresponds to a stable (equilibrium) geometric configuration and thus to a minimum on the adiabatic potential surface, i.e., to a minimum on the total energy function of the form $E_T = E_T(R_a,R_e)$. It seems that depending on the nature of the actual ligand sphere with the same chromophore, e.g., CuO_6, the minimum on the adiabatic potential surface moves along a smooth curve, i.e., along the R_a vs. R_e correlation curve. The stronger is the "perturbation" associated with an actual ligand, the larger is the displacement (measured for example with the tetragonality parameter[1-3]) from the pseudooctahedral configuration. In the first approximation this effect can be rationalized in terms of the cis influence: the change of equatorial ligands has an influence on the cis direction, i.e., on the axial distance R_a. However, also the chromophore CuF_6 exhibits an R_a vs. R_e dependence similar to that for CuO_6, CuN_6, and CuN_4O_2 as will be shown in the next section. In this case the cis influence is to be ruled out from consideration because a "perturbation" can be caused only by the cationic part of the crystal.

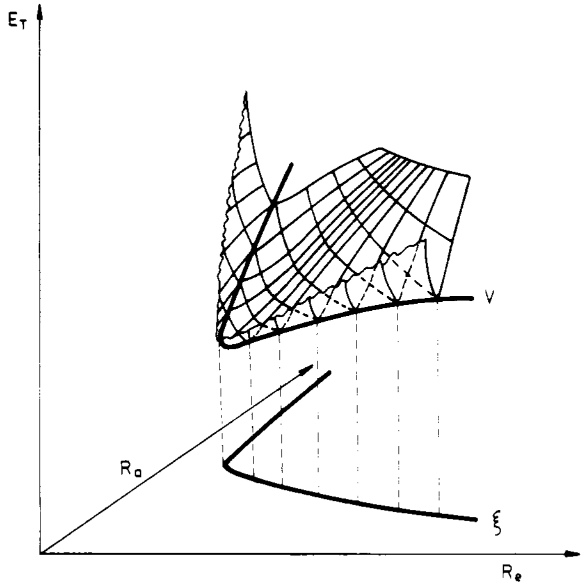

Figure 1. Schematic representation of a valley, V, in the adiabatic potential surface $E_T(R_a,R_e)$. ξ is the R_a vs. R_e correlation curve.

Results and Discussion

Let us consider reaction 1 or Chart I. The analysis of

$$\underset{D_{4h}}{CuF_4^{2-}} \xrightarrow{+2F^-} \underset{D_{4h}}{CuF_6^{4-}} \rightarrow \underset{O_h}{CuF_6^{4-}} \rightarrow \underset{D_{4h}}{CuF_6^{4-}} \xrightarrow[-4F^-]{} \underset{D_{\infty h}}{CuF_2} \quad (1)$$

experimental data shows (Table I) that Chart I partially realized. Thus an existence of the R_a vs. R_e correlation is indicated here also for the chromophore CuF_6. The crucial question at this point can be formulated as follows: In the CuF_6^{4-} ion does an intrinsic disposition exist to follow the R_a vs. R_e dependence? Or in other words, does the adiabatic potential surface in the CuF_6^{4-} ion exhibit a valley, V, the projection of which on the $\{R_a,R_e\}$ plane with the R_a vs. R_e correlation function, ξ, is coincident (Figure 1)?

The problem was solved by applying quantum chemical computational methods. Actually, the CNDO/2 version of semiempirical all-valence MO–LCAO–SCF calculations was used.[23] First a mapping of the adiabatic potential surface was

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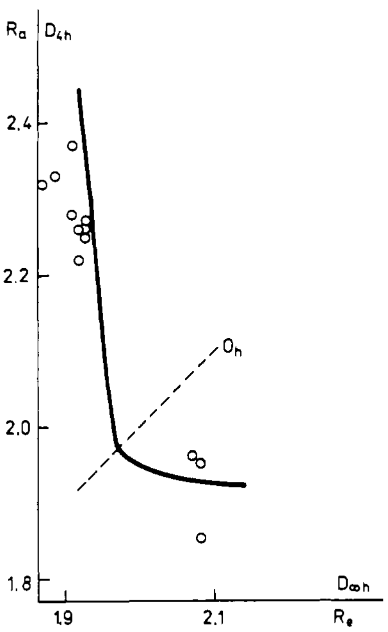

Figure 2. Calculated R_a vs. R_e correlation curve for CuF_6^{4-}: O, experimental points.

made; namely, the total molecular energy, E_T, of the complex CuF_6^{4-} was calculated for the pairs of R_a and R_e which vary independently by the step of 0.005 nm. The equilibrium geometry of a limit case, square-planar CuF_4^{2-}, can easily be obtained either from refining the variation step to localize the energy minimum or from the local minimum after a parabolic fitting of the cut of the adiabatic potential surface. Analogically, the optimum geometries of CuF_2 and of the octahedral CuF_6^{4-} were calculated.

The valley on the two-dimensional adiabatic potential surface was found according to the conception of the minimum energy coordinate proposed by Swanson.[27-30] Starting from the octahedral arrangement of CuF_6^{4-}, the coordinate R_a increases by a step, e.g., $\Delta R_a = 0.005$ nm. Then R_e is varied until the function E_T $(R_a^c(=\text{constant}),R_e)$ relaxes to a local minimum, where $(\partial E_T/\partial R_e)_{R_a^c} = 0$. The obtained local minima are connected with a smooth curve which approaches the optimum geometry of square-planar CuF_4^{2-} in the limit case of $R_a \to \infty$. Analogically, the second part of the valley (or R_a vs. R_e correlation curve) was obtained starting from the octahedral CuF_6^{4-}: R_e increases by a step of ΔR_e, and then R_a is varied until the function $E_T(R_e^c(=\text{constant}),R_a)$ relaxes to a local minium, where $(\partial E_T/\partial R_a)_{R_e^c} = 0$. The calculated two parts of R_a vs. R_e correlation curve (Figure 2) represent well the minimum energy path in the harmonic approximation.[27-30] The experimental points are also included in Figure 2, and it can be concluded that the theoretical curve is in a remarkable agreement with the experimental points.

The principal result of this note lies in the proof that the adiabatic potential surface in the CuF_6^{4-} ion exhibits a valley, the projection of which into the $\{R_a,R_e\}$ plane is coincident with the R_a vs. R_e correlation curve. Therefore in CuF_6^{4-} ion an intrinsic disposition exists to undergo distortions along an R_a vs. R_e dependence.[31] That valley represents a reaction path according to Chart I: it starts from CuF_4^{2-} and finishes at CuF_2. It seems that a "degree of conversion" according to Chart I depends on the cationic part of the crystal and the reaction can be stopped at certain points of ξ.

Table II. Fine Mapping of the Adiabatic Potential Surface $E_T(R_a,R_e)$ in the CuF_6^{4-} Ion[a]

	R_a					
R_e	1.95	1.96	1.97	1.98	1.99	2.00
2.01	0.47689	0.48778	0.48195	0.46001		
2.00	0.48421	0.49695	0.49294	0.47283		0.38672
1.99	0.48440	$\underline{0.49899}$	0.49683	0.47856	0.44477	
1.98	0.47718	0.49364	0.49335	0.47692	0.46774	
1.97		0.48056	0.48216	0.49150	0.48397	0.46023
1.96		0.45949	0.48803	0.49903	0.49315	0.47106
1.95	0.40788		0.48656	$\underline{0.49922}$	0.49501	0.47457
1.94			0.47743	0.49177	0.48923	0.47045

[a] Total energy $E_T(R_a,R_e) = -5226.0 - E'$ (eV), where E' is listed in the table. R_a and R_e are in 10^{-10} m. Energy minima are underlined.

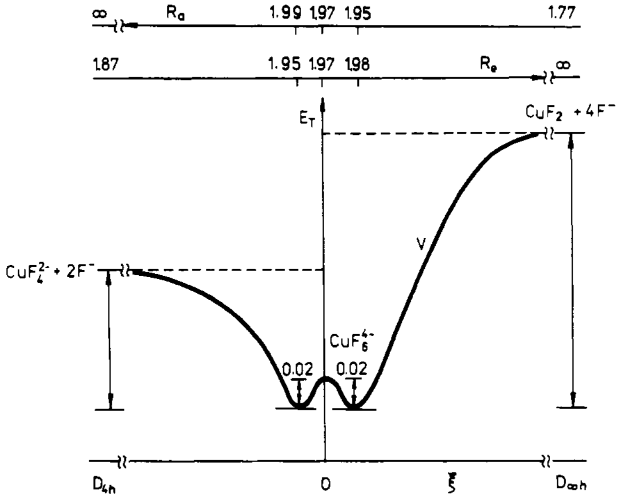

Figure 3. Shape of a valley, V, with two minima in CuF_6^{4-}.

Finally, it must be pointed out that the octahedral CuF_6^{4-} ion has a doubly degenerated electronic ground term ^2E_g and in agreement with the Jahn–Teller theorem the adiabatic potential surface has no minimum in this nuclear configuration.[33] The fine mapping of the adiabatic potential surface (Table II) shows that there are two minima corresponding to a flattened and an elongated octahedron. Then after refinement the valley V has the form as shown in Figure 3. Thus conclusions following from the Jahn–Teller theorem[34] are implicitly included in the calculated shape of the adiabatic potential surface.

Registry No. CuF_6^{4-}, 20581-14-0.

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(31) Strictly speaking, the above procedure represents only one approach in order to explain a tendency of Cu(II) complexes being rather tetragonal than octahedral. Alternatives can be found in the literature[3,32] and often a qualitative picture is asked. Unlike to the angular overlap method or extended Hückel calculations the single-orbital energy analysis is not recommended for the CNDO method. A UHF approach used as well as the explicit inclusion of the nuclear repulsion term in the total energy expression makes the single-orbital energy analysis less conclusive. A more suitable approach seems to be an energy partitioning on one-center and two-center (the ligand–ligand and the metal–ligand) contributions. The last term appears to be crucial for the complex stabilization as reported elsewhere.[9]

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