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Rhodium Carboxylate Complexes of Diphenyltriazene and Berenil, a Substituted Triazene and DNA-Binding Ligand. Crystal and Molecular Structure of Tetrakis(μ-acetato)bis(diphenyltriazene)dirhodium(II)

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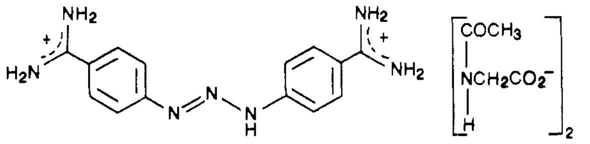
The crystal and molecular structure of the neutral adduct of diphenyltriazene (dptH) with rhodium acetate, $[Rh_2(O_2CCH_3)_4(dptH)_2]$, was determined. The title compound belongs to the triclinic space group $P\bar{1}$ with $a = 8.173$ (1) Å, $b = 8.923$ (2) Å, $c = 12.191$ (1) Å, $\alpha = 91.95$ (1)°, $\beta = 101.77$ (1)°, $\gamma = 101.54$ (1)°, $V = 850.2$ (4) Å^3, $d_{calcd} = 1.63$ g/m^3, $Z = 1$, and mol wt = 834.46. The structure was refined on 1978 observed reflections to $R = 0.077$. The structure contains linearly bound diphenyltriazene with Rh–N bond lengths of 2.301 (8) Å and N–N bond lengths of 1.27 (2) and 1.32 (2) Å, with an N–N–N angle of 114 (1)°. The planes of the phenyl rings in one diphenyltriazene ligand are puckered at a dihedral angle of 39.7°. The correlations between the structure and the IR spectra of this complex have been used to assign structures of complexes of rhodium carboxylates with Berenil, a DNA-binding ligand. In this latter case both linear and bridging examples have been identified.

The chemotherapeutic activity of transition-metal complexes such as *cis*-$[PtCl_2(NH_3)_2]$, cisplatin, is of current interest.[1] Recently we have surveyed the activity of metal complexes against *Trypanosoma rhodesiense*, responsible for sleeping sickness in man.[2] This work is relevant because, apart from the intrinsic interest in finding much-needed new drugs in parasitic diseases, there is a remarkable coincidence between drugs active in both trypanosomiasis and cancer[3,4] and activity was indeed found in the former case for complexes of platinum and ruthenium.[2] Comparisons between structural types active in both diseases may be useful in appointing promising areas for further investigation of metal-based drugs.

In this respect the observations that metalation of Berenil (4,4′-(1-triazene-1,3-diyl)dibenzamidine bis(*N*-acetylglycinate)[34] a known trypanocide,[5] gave in some cases complexes that were more active than the free drug are noteworthy.[2] Since Berenil is selectively toxic to the trypanosomes, it may be considered to be a metal-transport agent. Berenil presents an attractive ligand because (a) the mode of action is believed to be inhibition of DNA synthesis,[5] (b) the drug (ligand) binds to DNA in an outer-sphere manner by polar interaction between the amidine groups and the phosphate oxygens of the nucleic acid, and (c) there is a metal-binding site, the triazene bridge, distinct from the DNA-interacting part of the molecule.



To understand the factors affecting metal transport and potentiation of DNA-binding drugs by metals, an unequivocal picture of the structures of these complexes is necessary. In this work, we have found the study of analogous diphenyltriazene complexes to be very useful in structure assignment, and this paper reports on our studies of the reactions of Berenil and diphenyltriazene with rhodium carboxylates.

Experimental Section

Starting Materials and Physical Methods. Diphenyltriazene was obtained commercially and used without further purification. Berenil was a gracious gift from Hoechst Ltd. The rhodium carboxylates were prepared by standard procedures as the methanol adducts.[6]

IR spectra were recorded as KBr disks on a Perkin-Elmer 237 spectrophotometer. Elemental analyses were from Galbraith.

Table I. Crystallographic and Additional Data for $[Rh_2(O_2CCH_3)_4(dptH)_2]$

$C_{20}H_{34}N_6O_8Rh_2$	fw = 834.46
cryst size, mm	0.30 × 0.11 × 0.32
space group	triclinic $P\bar{1}$

a, Å	8.173 (1)	α, deg	91.95 (1)
b, Å	8.923 (2)	β, deg	101.77 (1)
c, Å	12.191 (1)	γ, deg	101.54 (1)
Z	1	V, Å^3	850.2 (4)
T, K	295	d_{calcd}, g/cm^3	1.63

diffractometer	Enraf-Nonius CAD-4
radiation	graphite-monochromatized Mo Kα, $\lambda = 0.070926$ Å
scan mode (limits, deg)	θ–2θ ($1 \le \theta \le 25$)
θ range, deg	1–25
$\pm h, \pm k, \pm l$ range	$h = \pm 9$, $k = \pm 9$, $l = 0$–13
total reflecns	2490
obsd reflecns	1978 with $I > 3\sigma(I)$
linear abs coeff, mm^{-1}	9.18
data redn	Lp corrections performed
R_i	0.057
R_{obsd}	0.077
R_{all}	0.097

Preparation of Complexes. Diphenyltriazene Complexes. The compound $[Rh_2(O_2CCH_3)_4(dptH)_2]$ was prepared by addition of diphenyltriazene (0.0197 g, 0.1 mmol) in 5 mL of MeOH to a saturated methanol solution of rhodium acetate (0.0253 g, 0.05 mmol) and the solution stirred overnight. Evaporation of the dark solution gave a red-brown solid, yield 77%, which upon recrystallization from CH_2Cl_2 gave dark red crystals suitable for crystallography. A similar reaction occurs with rhodium butyrate, but the extra solubility precludes recrystallization, the complex being very soluble even in diethyl ether. Anal. Calcd for $C_{40}H_{50}N_6O_8Rh_2$: C, 51.72; H, 5.39; N, 9.05. Found: C, 52.10; H, 5.5; N, 9.3.

Berenil Complexes. The compound $[Rh_2(O_2CCH_3)_4(Ber_n)_2]$ was prepared by addition of Berenil salt (0.057 g, 0.1 mmol) in 20 mL of hot MeOH to a methanolic solution of rhodium acetate (0.0253 g, 0.05 mmol). Stirring overnight followed by evaporation to half-volume and addition of diethyl ether gave a light green solid, yield 56%. Anal. Calcd for $C_{36}H_{42}N_{14}O_8Rh_2$: C, 43.02; H, 4.18; N, 19.52. Found: C, 42.83; H, 4.52; N, 20.10. The reaction with rhodium butyrate gave a similar green coloration, but upon evaporation the ligand precipitated preferentially and no complex was isolated.

The compound $[Rh_2(O_2CCH_3)_3(Ber_a)]$ was prepared in a similar manner but with the addition of Et_3N (1 mL). In this case stirring

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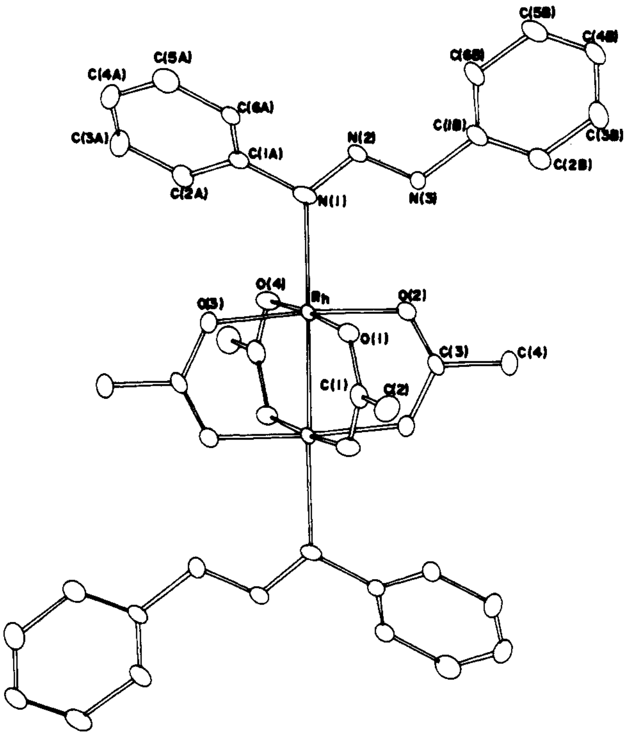


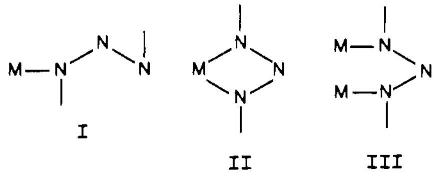
Figure 1. ORTEP digram of the molecule $[Rh_2(O_2CCH_3)_4(dptH)_2]$ showing atomic identification.

overnight gave a brown, very insoluble precipitate, which was filtered, washed with methanol and diethyl ether, and dried; yield 60%. Anal. Calcd for $C_{20}H_{23}N_7O_6Rh_2$: C, 36.19; H, 3.47; N, 14.8. Found: C, 36.43; H, 3.71; N, 15.10. The compound $[Rh_2(O_2C(CH_2)_2CH_3)_3(Ber_a)]$ was obtained in 70% yield. Anal. Calcd for $C_{26}H_{35}N_7O_6Rh_2$: C, 41.77; H, 4.69; N, 13.12. Found: C, 42.18; H, 5.1; N, 12.89.

Solution of the Structure. A reddish single crystal with dimensions 0.30 × 0.11 × 0.32 mm was selected by examination under polarized light and used on an Enraf-Nonius CAD-4 diffractometer for cell dimension measurements and intensity data collection at 23 °C. The crystal data are given in Table I. The structure was solved by Patterson and difference Fourier methods. The refinement was by a full-matrix least-squares method, with unit weights, minimizing the function $\sum w(k|F_o| - |F_c|)^2$ to a final value of $R = 0.077$ for the observed reflections and $R = 0.097$ for all reflections when the maximum LS shift to error was <1 and the largest peaks in the final difference Fourier synthesis were approximately 0.3 e Å^{-3}. Atomic scattering factors and anomalous dispersion terms were taken from ref 35. Hydrogen atoms were included in the structure factor calculations with their positional coordinates determined by geometrical bond considerations and a Debye-Waller factor taken as 6.0 Å^2 but not included in the refinement. The programs used were SDP and SHELX-79.

Results and Discussion

Triazenes may bind to metals in one of three distinct manners, similar to those of the isoelectronic carboxylates:



Examples of all three types (linear monodentate,[7] chelating bidentate,[8,9] and bridging bidentate[10-14]) have been structurally characterized. In form II the N–N–N angle is approximately 105° and in comparison to the other two forms is sterically unfavorable. For square-planar complexes the tendency is for the bridging mode, and this has been exploited to prepare mixed-metal species from linear triazenes as precursors.[15,16] Neutral triazenes are rare,[17] due in part to the use of forcing conditions, e.g. base, in the synthesis. The stepwise synthesis of $[Pd_2(dpt)_4]$ from $[Pd(dptH)_2Cl_2]$ has been described in agreement with these points.[16]

Table II. Fractional Atomic Coordinates for the Non-Hydrogen Atoms of $[Rh_2(O_2CCH_3)_4(dptH)_2]^a$

atom	x/a	y/b	z/c	B_{eq}
Rh	0.5619 (2)	0.5629 (1)	0.5923 (1)	2.64 (3)
O(1)	0.763 (1)	0.459 (1)	0.5959 (7)	3.5 (3)
O(2)	0.435 (1)	0.374 (1)	0.6553 (7)	3.9 (3)
O(3)	0.682 (1)	0.7410 (9)	0.5175 (8)	3.5 (3)
O(4)	0.351 (1)	0.657 (1)	0.5760 (8)	3.5 (3)
C(1)	0.762 (2)	0.372 (2)	0.511 (1)	3.3 (4)
C(2)	0.919 (2)	0.304 (2)	0.515 (1)	4.3 (5)
C(3)	0.346 (2)	0.264 (2)	0.589 (1)	3.1 (4)
N(1)	0.312 (2)	0.313 (1)	0.2334 (1)	3.7 (4)
N(2)	0.273 (2)	0.369 (1)	0.1399 (9)	3.8 (4)
N(3)	0.341 (2)	0.517 (1)	0.1407 (9)	3.9 (4)
C(1A)	0.238 (2)	0.151 (2)	0.224 (1)	3.0 (4)
C(2A)	0.332 (2)	0.058 (2)	0.286 (1)	4.2 (5)
C(3A)	0.275 (2)	−0.096 (2)	0.276 (1)	4.2 (5)
C(4A)	0.117 (3)	−0.163 (2)	0.208 (2)	5.6 (6)
C(5A)	0.019 (2)	−0.071 (2)	0.147 (1)	5.4 (5)
C(6A)	0.081 (2)	0.091 (2)	0.156 (1)	4.5 (5)
C(1B)	0.317 (2)	0.584 (2)	0.035 (1)	3.9 (4)
C(2B)	0.427 (2)	0.726 (2)	0.032 (1)	5.1 (5)
C(3B)	0.407 (3)	0.794 (2)	−0.068 (2)	5.9 (6)
C(4B)	0.295 (3)	0.727 (2)	−0.162 (1)	5.9 (6)
C(5B)	0.189 (3)	0.589 (2)	−0.156 (1)	6.9 (7)
C(6B)	0.202 (3)	0.515 (2)	−0.057 (1)	6.4 (6)

[a] Esd's are given in parentheses. The B_{eq} (Å^2) values are the equivalent isotropic temperature factors: $B_{eq} = {}^4/_3\sum_{ij}T_{ij}B_{ij}$.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) in $[Rh_2(O_2CCH_3)_4(dptH)_2]^a$

Rh–Rh′	2.407 (2)	Rh–N (1)	2.301 (8)
Rh–O(1)	2.037 (9)	N(1)–N(2)	1.27 (2)
Rh–O(2)	2.050 (9)	N(2)–N(3)	1.32 (2)
Rh–O(3)	2.040 (9)	N(1)–C(1A)	1.44 (2)
Rh–O(4)	2.042 (9)	N(3)–C(1B)	1.43 (2)
Rh–Rh′–N(1)	178 (1)	Rh–N(1)–N(2)	129 (1)
O(1)–Rh–O(2)	89.6 (7)	N(1)–N(2)–N(3)	114 (1)
O(1)–Rh–O(3)	89.6 (5)	Rh–N(1)–C(1A)	120 (1)
O(1)–Rh–O(4)	175.2 (8)	C(1A)–N(1)–N(2)	110 (1)
O(1)–Rh–N(1)	91 (9)	N(2)–N(3)–C(1B)	117 (1)
O(1)–Rh–Rh′	88.2 (6)		

[a] Esd's are given in parentheses.

To help in assignment of the structures of the Berenil complexes, similar reactions were carried out with the parent triazene. The reaction of neutral diphenyltriazene with rhodium acetate in methanol gave a dark red solid that was analyzed as $[Rh_2(O_2CCH_3)_4(dptH)_2]$ with the presence of ν(NH) in the IR spectrum indicating a neutral triazene. Recrystallization from dichloromethane gave dark red crystals suitable for structural analysis, and to ascertain the mode of binding, an X-ray crystal structure determination was carried out.

Description of the Structure of $[Rh_2(O_2CCH_3)_4(dptH)_2]$. The unit cell contains only one discrete molecule, which presents an inversion center coincident with the crystallographic $P\bar{1}$ center. Due to this, the refinement was carried out on half of the molecule. Figure 1 is an ORTEP presentation of the molecule with atomic identification.

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Table IV. Structural Parameters for Rhodium Carboxylate Complexes with Nitrogen-Donor Axial Ligands

complex[a]	bond lengths, Å Rh–Rh	Rh–O	Rh–N	angle, deg Rh–Rh–N	ref
$[Rh_2(O_2CCH_3)_4(4\text{-}CNpy)]\cdot CH_3CN$	2.393 (1)	2.042 (3)	2.244 (4)	176.9 (1)	20
$[Rh_2(O_2CCH_3)_4(py)_2]$	2.3963 (2)	2.038 (2)	2.227 (3)	180.0 (0)	21
$[Rh_2(O_2CCH_3)_4(NHEt_2)_2]$	2.4020 (7)	2.037 (3)	2.301 (5)	176.6 (1)	22
$[Rh_2(O_2CCH_3)_4(dptH)_2]$	2.407 (2)	2.036 (3)	2.301 (8)	178 (1)	this work
$[Rh_2(O_2C_2CH_5)_4(acr)_2]$	2.417 (1)	2.036 (3)	2.413 (3)	178.86 (7)	23
$[Rh_2(O_2CC_2H_5)_4(7\text{-}azd))_2]$	2.403 (1)	2.039 (5)	2.266 (6)	175.2 (1)	23
$[Rh_2(O_2CC_2H_5)_4(phz)]$	2.409 (1)	2.040 (3)	2.362 (4)	174.71 (9)	23

[a] Abbreviations: py, pyridine; dptH, diphenyltriazine; acr, acridine; 7-azd, 7-azaimdole; phz, phenazine.

Table V. IR Data for Diphenyltriazene and Berenil Complexes of Rhodium Carboxylates[a]

complex	ν(NH)	ν(tri)
diphenyltriazene	3180	1245 (m), 1200 (s) 1175 (s), 1140 (w)
$[Rh_2(O_2CCH_3)_4(dptH)_2]$	3180	1260 (s), 1205 1170 (s), 1160 (sh)
Berenil (salt form)	3150 (w) 3300 (br)[b]	1290 (m), 1260 (s) 1190 (sh), 1175 (s)
$[Rh_2(O_2CCH_3)_4(Ber_n)_2]$	3120 3300 (br)	1295 (m), 1265 (s) 1190 (sh), 1170 (s)
$[Rh_2(O_2CCH_3)_3(Ber_a)]$	3300 (br)	1250 (s, br), 1200 (w) 1165 (s)
$[Rh_2(O_2CC_3H_7)_3(Ber_a)]$	3300 (br)	1255 (s, br), 1200 (w) 1170 (s)

[a] In cm^{-1} as KBr disks. [b] ν(NH) of amidine groups.

Final positional and equivalent isotropic thermal parameters are listed in Table II, and anisotropic thermal parameters are available as supplementary material as well as the complete list of observed and calculated structure amplitudes. Distances and important interatomic angles are given in Table III.

The two triazene ligands are bound to the metal through only one nitrogen atom. This monodentate configuration of both triazene ligands was first confirmed in *cis*-$[Pt(PPh_3)_2(dpt)_2]$.[7] The N–N bond lengths have nearly equal values (1.27 (2) and 1.32 (2) Å), the bond nearest the metal being shortest. This is in contrast to the case for the platinum complex (1.336 (6) and 1.2786 (6) Å), where the bond nearest the metal is longer. The canonical structure for a neutral triazene has the double bond adjacent to the metal with the hydrogen on the farthest nitrogen, and so the differences can be explained, although in both cases significant delocalization is apparent. The N–N–N angle of 114 (1)° is consistent with the reported values in the platinum complex.[7] The bond lengths and angles found in the phenyl rings do not differ significantly from the accepted values of 1.39 Å and 120°, respectively. The dihedral angle between the planes of the two phenyl rings is 39.7°. The same puckering occurs in one of the triazenido ligands of the platinum complex, the angle being 43.2°.

The parameters for the rhodium acetate cage show no major deviations from those reported in the many complexes studied of this system.[18,19] Table IV summarizes pertinent data with other nitrogen donor axial ligands. The Rh–Rh distance is in good agreement with those previously reported, and the Rh–N distance (2.301 Å) falls between the shorter value for pyridine (2.227 Å) and the relatively longer one for a weak donor such as acridine (2.413 Å). The complex is the first structurally characterized of a neutral, linear triazene.

Spectroscopic Data. The IR data are summarized in Table V. The criteria for assignment of triazene binding by IR spectroscopy have been discussed.[24,25] Knoth[24] divided triazenes into two classes distinguished by their spectra: class A, showing two bands at 1260–1300 and 1580–1600 cm^{-1}, was considered indicative of a chelate whereas class B, with four absorptions at 1150, 1190–1210, 1260–1300, and 1580–1600 cm^{-1}, consisted of both linear and bridging examples. The 1100–1300-cm^{-1} region may distinguish all types, although the presence of triphenylphosphine in many of the complexes studied[24,25] means that the interpretation is not unambiguous.

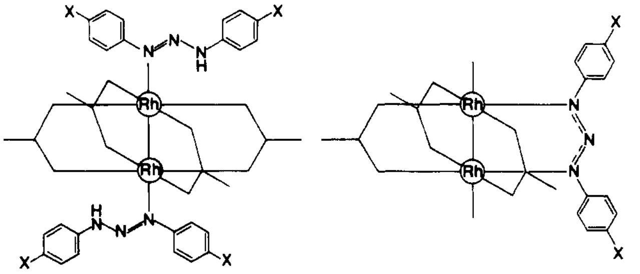

Figure 2. Structures of (left) neutral, linear (X = H, $C(NH)(NH_2)$) and (right) anionic bridging triazene (X = $C(NH)(NH_2)$) complexes of rhodium carboxylates.

Free diphenyltriazene shows bands at 1245 (s), 1200 (s), 1175 (s), 1160 (w), and 1140 cm^{-1}, which in the rhodium acetate adduct are reduced to four at 1260, 1205, 1170, and 1160 (sh) cm^{-1}. No bands due to rhodium acetate are in this region, allowing for the unequivocal assignment of all bands as due to the triazene skeleton, these bands may therefore be considered indicative of a linear triazene.

The IR spectrum of the neutral Berenil adduct shows bands at 1295, 1265, 1190 (sh), and 1170 cm^{-1}, whereas in the free ligand these appear at 1290, 1260, 1190, and 1175 cm^{-1}, again with the same relative intensities, and so an identical structure assignment can be made, with two Berenil molecules occupying the axial positions. The absence of carboxylate bands of *N*-acetylglycine also confirms that no counteranion is present. The ^1H NMR spectrum of the adduct also shows no acetylglycine and the expected intensity ratios. The complex is probably best described as a weak adduct of the basic cage structure; the easy displacement with adenine (see below) and the fact that the more soluble butyrate analogue does not form the neutral adduct are evidence to the weak nature of the adduct, and this may explain the color of the complex. In fact, in a separate study of amine complexes of rhodium carboxylates we have noticed a large difference in lability in aqueous solution for the various carboxylates—the *n*-$PrNH_2$ adduct of rhodium acetate is quite stable, whereas the propionate analogue discolors to the aquo adduct almost immediately.

When Berenil is allowed to react under conditions of formation of the anion, complexes are formed whose elemental analyses indicate the displacement of one carboxylate by a triazene. These complexes (both for the acetate and butyrate) show no ν(NH) band of the triazene and two strong, broad bands at ~1250 and ~1170 cm^{-1} with a weak pair at 1200 cm^{-1}, distinctly different from the previous example. The binding mode is then bridging.

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We eliminate possible binding of the amidine in this case because of the changes in the triazene frequencies and also the fact that the frequencies attributed to the amidine moiety (ν(CN) = 1625 cm^{-1} (br)) remain unaltered in all samples. The structures are therefore shown in Figure 2.

A reviewer has suggested that oxidation of the cage structure by the amidine moiety is a possibility. In separate experiments we have been examining the EXAFS spectra of these complexes.[26] Although EXAFS may not distinguish between neighboring atoms such as N and O, it can give very accurate M–M distances, and we have studied the Rh carboxylate–adenine system.[27] The Rh–Rh distances for both the neutral and bridged Berenil complexes are slightly longer than for the parent complexes (for $[Rh_2(OAc)_3(Ber_a)]$ a value of 2.432 Å is obtained compared to 2.395 Å for $[Rh_2(OAc)_4(caffeine)_2]$, which we used as a standard[27] and whose crystal structure has been determined[28].) The mixed-valence dimer $[Rh^{II}Rh^{III}(OAc)_4]^+$ has a slightly shorter Rh–Rh bond of 2.318 Å, as expected.[29] These data, plus analysis of the edge EXAFS spectra, confirm that the oxidation state is Rh(II) and no oxidation has occurred.

A further point to be addressed is the solid-state nature of the bridged complexes, which may be polymeric, accounting for their insolubility. The molecular unit, however, must be the structure proposed with bridging triazene and possibly a polymeric network of amidine groups hydrogen-bonding to the oxygens of the carboxylate ligands. The neutral diphenyltriazene adduct has been reported briefly, and it was observed that, even in the presence of base, the neutral adduct rather than the bridged adduct was formed.[18] We have noted similar behavior, and the isolation of the bridged Berenil complexes is probably due to their insolubility, resulting in preferential precipitation from solution.

Biological Relevance. In our survey of metal complexes in *T. rhodesiense* we included rhodium carboxylates because of their reported antitumor activity[30] although the complexes appear too toxic for further development. The simple carboxylate complexes do not show any activity in *T. rhodesiense*, but all Berenil complexes are active, both in vitro and in vivo.[2,31] However, in L1210, a standard screen for antitumor activity, rhodium butyrate is significantly more active than the Berenil-substituted derivative.[32] Thus, a situation is emerging where the relative specificity of two closely related species is affected by the activity of the carrier group:

L1210 $[Rh_2(OBu_4)] > [Rh_2(OBu)_3(Ber_a)]$

but

T. rhodesiense $[Rh_2(OBu)_3(Ber_a)] > [Rh_2(OBu)_4]$

Whether these differences are due to differential absorption or reflect differences in binding to biological substrates (e.g. DNA) is under investigation. The neutral Berenil adduct reacts with nucleic acid bases such as adenine (Ade) by displacement, giving the known 1:1 adducts $[Rh_2(O_2CR)_4(Ade)]$;[33] the anionic, bridging complexes react in a manner similar to that for the parent carboxylates, by adduct formation. The structural characterization of different modes of binding also allows for structure–activity relationships and extension to the more complicated platinum case.[2]

Conclusions. The crystal and molecular structure of $[Rh_2(O_2CCH_3)_4(dptH)_2]$ has been determined and the linear mode of binding of the neutral triazene confirmed. In conjunction with IR data the modes of binding of rhodium carboxylate complexes with Berenil, a DNA-binding ligand, have also been confirmed by analogy.

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Supplementary Material Available: Tables of fractional atomic coordinates for hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms, complete listings of bond distances and angles, and a stereoscopic view of the unit cell contents (5 pages); a complete listing of *hkl*, F_o, and F_c (8 pages). Ordering information is given on any current masthead page.

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