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Ruthenium(IV) in Centrosymmetric $RuX_2N_2O_2$ Coordination: Synthesis, Structure, and Redox Properties of Dihalobis(triazene 1-oxidato)ruthenium Species

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The reaction of tris(1-alkyl-3-aryltriazene 1-oxidato)ruthenium(III), RuT_3, with concentrated aqueous HX or gaseous HX (X = Cl, Br) yields crystalline RuX_2T_2. The structure of dichlorobis(1-ethyl-3-*p*-tolyltriazene 1-oxidato)ruthenium(IV) has been determined X-ray crystallographically. The crystal is monoclinic, $P2_1/n$, and has the unit cell dimensions a = 9.824 (4) Å, b = 17.059 (7) Å, c = 6.564 (3) Å, β = 99.57 (1)°, V = 1085 (2) Å^3, and Z = 2. The coordination sphere is $RuCl_2N_2O_2$, with the metal atom located at the center of symmetry. The chelate dimensions are normal, and the phenyl ring is only slightly (10°) tilted from the chelate-ring plane. The Ru–Cl distance is 2.367 (1) Å. The complexes display strong absorption bands at relatively low energies (800–1000 nm) that are assigned to T → Ru(IV) charge transfer. The formal potential of the redox couple $Ru^{IV}X_2T_2 + e^- \rightarrow [Ru^{III}X_2T_2]^-$ lies in the range 0.1–0.2 V vs. SCE in acetonitrile (voltammetry at platinum). Thus, RuX_2T_2 is a relatively weak oxidant. The ruthenium(III) species $Ru^{III}X_2T_2^-$ can be reduced further in a one-electron process presumably to unstable $Ru^{II}X_2T_2^{2-}$. Left to itself, $Ru^{III}X_2T_2^-$ forms a dimeric species having characteristic voltammetric responses.

Introduction

In contrast to the +2 and +3 oxidation states, the +4 state of ruthenium has thus far afforded only a limited number of well-defined discrete molecular species.[2,3] These include halo complexes—K_2RuCl_6 being the prototype—and their derivatives,[4,6] certain organometallic[7-10] and hydridic[11] substances, some dithiocarbamates,[12-15] and species having the Ru=O moiety bound to unsaturated nitrogeneous ligands.[16,17] Our interest in ruthenium(IV) compounds is aroused by their paucity as well as by their possible relevance in catalytic processes and mechanisms.[7-9,16,17]

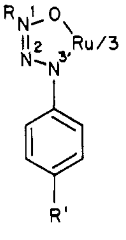
It was shown[18,19] recently that tris(triazene 1-oxidato)ruthenium(III) (**1**; RuT_3) displays the electrochemically reversible redox process (1) in the range 0.2–0.7 V vs. the saturated calomel electrode (SCE). Attempts to isolate the rutheni-

$$Ru^{IV}T_3^+ + e^- = Ru^{III}T_3 \qquad (1)$$

um(IV) cation as salts have been unsuccessful so far. We accidently discovered[20] that the reaction of RuT_3 with hydrochloric acid furnishes a crystalline compound of composition $RuCl_2T_2$, which has ruthenium in the formal oxidation state +4. The present work concerns this new group of complexes **2**–**5** as well as a bromide analogue **6**. The structure of one of the complexes (**2**) has been determined by using X-ray diffraction. The redox properties of the new complexes are of obvious interest and have been examined in detail.

Table I. Selected Bond Distances and Angles in $RuCl_2T_2$

	Bond Distances, Å		
Ru(1)–Cl(1)	2.367 (1)	O(1)–N(1)	1.311 (6)
–O(1)	1.974 (4)	N(1)–N(2)	1.288 (6)
–N(3)	2.007 (4)	N(2)–N(3)	1.321 (6)
	Bond Angles, deg		
Cl(1)–Ru(1)–O(1)	87.7 (1)	Ru(1)–O(1)–N(1)	112.2 (3)
–O(1)′	92.3 (1)	O(1)–N(1)–N(2)	121.5 (4)
–N(3)	93.2 (1)	N(1)–N(2)–N(3)	112.7 (4)
–N(3)′	86.8 (1)	Ru(1)–N(3)–N(2)	115.2 (3)
O(1)–Ru(1)–N(3)	77.3 (2)	Ru(1)–N(3)–C(1)	132.3 (4)



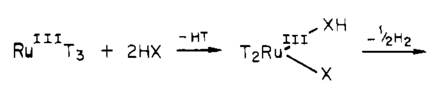
RuT_3

RuX_2T_2

	R	R′	X
2	Et	Me	Cl
3	Et	H	Cl
4	Et	Cl	Cl
5	Me	H	Cl
6	Me	H	Br

Results and Discussion

A. Synthesis. The conversion of RuT_3 to RuX_2T_2 occurs smoothly in good yield on treating a benzene solution of the former with concentrated aqueous HX or gaseous HX. The dark-colored crystalline complexes dissolve in polar organic solvents (CH_2Cl_2, MeCN, etc.), giving nonelectrolytic yellow-green solutions. The mechanism of the synthetic reaction is unclear. The sequence (2) is plausible. The key step is the



$$Ru^{III}T_3 + 2HX \xrightarrow{-HT} T_2Ru^{III}\!\begin{smallmatrix} \diagup XH \\ \diagdown X \end{smallmatrix} \xrightarrow{-\frac{1}{2}H_2} Ru^{IV}X_2T_2 \qquad (2)$$

transfer of one electron from ruthenium(III) to bound HX with concomitant homolytic cleavage of the HX bond. In a related reaction the involvement of chlorine radical has been postulated.[12]

B. Solid-State Structure of 2. Unit cell constants and systematic absences led to unique identification of the monoclinic space group $P2_1/n$, with Z = 2. To accommodate

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(1) (a) Indian Association for the Cultivation of Science. (b) Texas A&M University.
(2) Griffith, W. P. "The Chemistry of the Rarer Platinum Metals"; Wiley-Interscience: New York, 1967.
(3) Seddon, K. R. *Coord. Chem. Rev.* **1981**, *35*, 43; *Ibid.* **1982**, *41*, 79.
(4) Deloume, J. P.; Faure, R.; Thomas-David, G. *Acta Crystallogr., Sect. B* **1979**, *B35*, 558.
(5) Dwyer, F. P.; Goodwin, H. A.; Gyarfas, E. C. *Aust. J. Chem.* **1963**, *16*, 42.
(6) Dehand, J.; Rose, J. *J. Chem. Res. Synop.* **1979**, 155; *Inorg. Chim. Acta* **1979**, *37*, 249.
(7) Nicholson, J. K.; Shaw, B. L. *J. Chem. Soc A* **1966**, 807.
(8) Lydon, J. E.; Truter, M. R. *J. Chem. Soc. A* **1968**, 362.
(9) Colombo, A.; Allegra, G. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1653.
(10) Nowell, I. W.; Tabatabaian, K.; White, C. *J. Chem. Soc., Chem. Commun.* **1979**, 547.
(11) Hazeldine, R. N.; Malkin, L. S.; Parish, R. V. *J. Organomet. Chem.* **1979**, *182*, 323.
(12) Given, K. W.; Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1976**, *15*, 3152.
(13) Mattson, B. M.; Pignolet, L. H. *Inorg. Chem.* **1977**, *16*, 488.
(14) Wheeler, S. H.; Mattson, B. M.; Miessler, G. L.; Pignolet, L. H. *Inorg. Chem.* **1978**, *17*, 340.
(15) Miessler, G. L.; Pignolet, L. H. *Inorg. Chem.* **1979**, *18*, 210.
(16) Moyer, B. A.; Thompson, M. S.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 2310.
(17) Goswami, S.; Chakravarty, A. R.; Chakravorty, A. *J. Chem. Soc., Chem. Commun.* **1982**, 106.
(18) Mukherjee, R. N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1983**, 955.
(19) Mukherjee, R. N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.*, in press.
(20) Subsequently we found that an analogous reaction is reported for ruthenium dithiocarbamates.[11]

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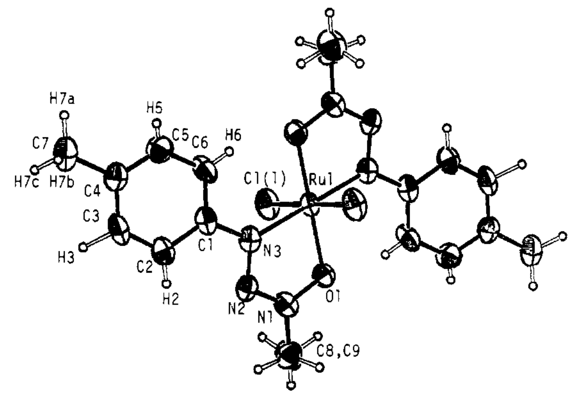


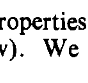
Figure 1. ORTEP drawing of the molecular structure of *trans*-$RuCl_2T_2$, T = $CH_3C_6H_4NNN(Et)O$ (**2**). All non-hydrogen atoms are represented by their ellipsoids of thermal vibration at the 40% probability level. Hydrogen atoms are represented by arbitrarily small spheres for the sake of clarity.

a molecule of composition **2**, it must reside on a crystallographic inversion center and it is thus required to have a trans,trans,trans geometry. This structural model is confirmed by successful refinement. Selected bond distances and bond angles are reported in Table I, and a view of the molecule is shown in Figure 1.

The ruthenium coordination sphere is grossly octahedral $RuCl_2N_2O_2$. The largest angular deviations from the idealized geometry, observed in the O–Ru–N angles, can be rationalized by constraints imposed by the triazene 1-oxide backbone. In particular, the chelate angle is 77.3°. The five-membered chelate rings are highly planar. Deviations from a mean plane passing through the origin (and thus containing both chelate rings related by the inversion center) are less than 0.07 Å. The dihedral angle between the chelate-ring plane and the corresponding phenyl ring is 10.6°, indicating a possible extention of the conjugation over the entire π system. Each ethyl group has a staggered conformation.

The Ru–Cl distance in **2** is 2.367 (1) Å, which is somewhat longer than that[4] in K_2RuCl_6 (2.318 Å). The Ru–Cl distances in $K_4Ru_2Cl_{10}O$, another octahedrally coordinated ruthenium(IV) compound, are 2.317 (7) and 2.363 (2) Å for the axial and equatorial bonds, respectively.[4] The molecular parameters for two organometallic species[8,9] and two dithiocarbamate species[11,14] are known. In all of these, Ru–Cl bonds are present, the metal coordination number is 7, and the terminal Ru–Cl distances lie within the range 2.43 ± 0.04 Å. We note that RuX_2T_2 constitutes the first authentic example of chelated ruthenium(IV) in centrosymmetric hexacoordination.

The structures of two other triazene 1-oxide complexes, one of nickel(II)[21] and one of cobalt(II),[22] are known. The dimensions of the chelate rings in these species are comparable to those in **2**. In all the cases the chelate bite angle lies within the range 80 ± 4°. The N(1)–N(2) distance is also substantially shorter than the N(2)–N(3) distance in all cases, which suggests that the contribution of the possible resonance structure **7** is relatively small in complexes of this group of ligands.



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The spectral and other properties of all RuX_2T_2 complexes are very similar (see below). We conclude that the trans,trans,trans structure is a characteristic feature of the entire group of complexes. All complexes are diamagnetic in the solid state as well as in solution (^1H NMR; see below). The presence of considerable tetragonal splitting and the ground-state configuration $(d_{xz}, d_{yz})^4(d_{xy})^0$ are indicated.

Table II. Visible-Ultraviolet and Microanalytical Data

	vis-UV[a]	analysis,[b] %		
compd	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	C	H	N
2	930 (11 650), 820 sh (6200), 540 (400), 415 sh (4600), 350 (10 200), 350 (12 600)	40.97 (40.92)	4.65 (4.58)	16.01 (15.91)
3	910 (8700), 810 sh (5800), 550 (250), 400 sh (4150), 395 sh (9400), 295 (9785)	38.57 (38.41)	4.08 (4.02)	16.92 (16.80)
4	930 (12 750), 810 sh (8000), 550 (170), 410 sh (4900), 350 sh (11 400), 300 (10 730)	33.73 (33.76)	3.25 (3.19)	15.01 (14.77)
5	910 (10 900), 810 sh (7000), 410 sh (4700), 350 sh (8200), 300 (17 770), 250 (19 740)	35.45 (35.61)	3.53 (3.42)	17.81 (17.80)
6	940 (6000), 820 sh (3000), 700 (2200), 410 sh (4200), 305 (14 200), 230 (19 000)	30.03 (29.97)	2.78 (2.87)	15.10 (14.98)

[a] In MeCN. Measurements were also made in CH_2Cl_2 and selected results are as follows: **2**, 940 (11 650), 810 sh (5360), 550 (700), 420 sh (4800), 360 (8190), 305 (13 780); **5**, 925 (13 900), 810 sh (8700), 550 (700), 410 sh (5400), 350 (8550), 300 (17 220), 260 (15 340). [b] Calculated values are in parentheses.

C. Spectra. The complexes display characteristic[18,19] vibration frequencies of the N_3 (1400–1550 cm^{-1}) and N–O (~1200 cm^{-1}) fragments. The bands are somewhat shifted to lower frequencies compared to those[18] of RuT_3. Complexes **2**–**5** have two or three sharp bands in the range 350–300 cm^{-1}; this has prevented the identification of the Ru–Cl stretch. All complexes exhibit expected ^1H NMR spectra in $CDCl_3$. Thus, **5** and **6** have single sharp Me signals at 5.15 and 5.05 ppm, respectively. In the corresponding CoT_3 complexes the Me signals appear[23] in the range 3–4 ppm. The low-field shift in RuX_2T_2 shows that the metal is highly oxidized. The electronic spectra of the complexes were measured in the range 1500–250 nm in dichloromethane and acetonitrile. Representative results are in Table II and Figure 2. The most characteristic feature is a rather strong band in the region 900–950 nm, which has a shoulder at ~800 nm. A T → Ru charge-transfer assignment is plausible. Significantly both[18,19] RuT_3 and $RuT(bpy)_2^{2+}$ display a similar absorption band, but at lower energies (650–750 nm); in these two cases the metal oxidation state is +3 (bpy = 2,2′-bipyridine). When the metal oxidation state is further reduced to +2, as in $RuT(bpy)_2^+$, the dominant spectral feature is the bpy → Ru transition (~500 nm).[19]

D. Redox Chemistry. In acetonitrile solution RuX_2T_2 compounds have molar conductances generally in the range 3–5 Ω^{-1} cm^{-2} mol^{-1}, showing that halide dissociation is virtually absent. The redox activity of RuX_2T_2 has been examined in this solvent (0.5 M in TEAP; 298 K) by using voltammetric techniques at a platinum working electrode. A well-behaved cyclic response is observed in the region 0.1–0.2 V vs. SCE. The peak-to-peak separation is 60 mV in all cases examined, and the peak height increases as $v^{1/2}$ where v is the scan rate. Coulometry performed at potentials negative to the cathodic peak potential shows that the electrode reaction has one-electron stoichiometry (n = 1). Electrochemical data are reported in Table III and shown in Figure 3, which also in-

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(21) Rajasekharan, M. V.; Varughese, K. I.; Manoharan, P. T. *Inorg. Chem.* **1979**, *18*, 2221.

(22) Dwivedi, G. C.; Srivastava, R. C. *Acta Crystallogr., Sect. B* **1971**, *B27*, 2316.

(23) Chakravorty, A.; Behera, B.; Zacharias, P. S. *Inorg. Chim. Acta* **1968**, *2*, 85. Behera, B.; Chakravorty, A. *Ibid.* **1972**, *4*, 372.

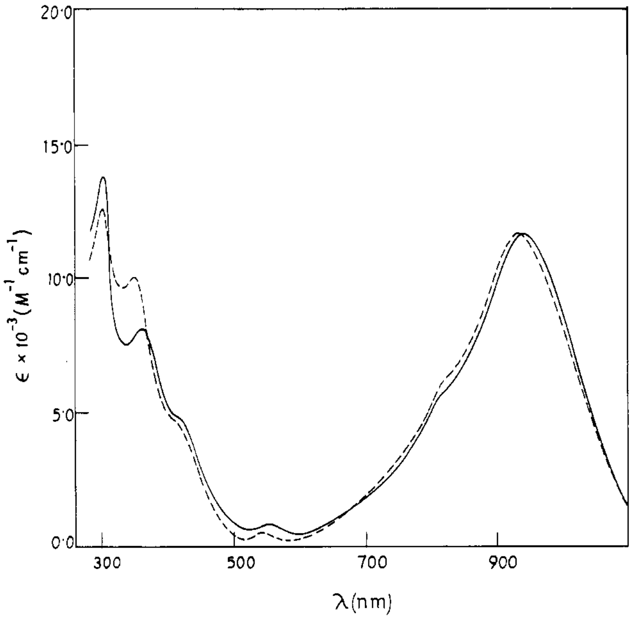

Figure 2. Electronic spectra in dichloromethane solution (—) and in acetonitrile solution (---) of $RuCl_2T_2$.

Table III. Electrochemical Data[a]

compd	Ru(IV)/ Ru(III)[b-d] E°_{298}, V (ΔE_p, mV)	Ru(III)/ Ru(II)[e,f] E_{pc}, V	n[g]
2	0.11 (60)	−1.52	0.94
3	0.15 (60)	−1.40	0.97
4	0.10 (80)	−1.45	1.05
5	0.19 (60)	−1.36	0.95
6	0.21 (60)	−1.25	1.02

[a] Unless otherwise stated, conditions are as follows: solvent, MeCN (0.1 M in tetraethylammonium perchlorate); electrode Pt; temperature 298 K; standard SCE. [b] Cyclic voltammetric data at scan rate of 50 mV s^{-1}. E°_{298} is calculated as the average of anodic and cathodic peak potentials. [c] Cyclic voltammetry was also done in CH_2Cl_2; selected results are as follows: **2**, 0.05 (250); **3**, 0.10 (200); 4, 0.11 (100). [d] Differential-pulse voltammetry (scan rate 10 mV s^{-1}; modulation amplitude 25 mV; droptime 0.5 s). Representative E°_{298} values in CH_2Cl_2 are as follows: **2**, 0.08; **4**, 0.11 in MeCN: **6**, 0.25 V. [e] E_{pc} is the cyclic voltammetric cathodic peak potential. [f] E_{pc} values in CH_2Cl are as follows: **3**, −1.62; 4, −1.60; **5**, −1.45; **6**, −1.36. [g] Determined coulometrically by using 0.01 mmol of solute in acetonitrile; reduction performed by holding the potential in the range −0.2 to −0.4 V.

cludes the differential-pulse voltammogram of one complex. The electrode process (3) thus represents a nearly ideal one-

$$RuX_2T_2 + e^- \rightarrow Ru^{III}X_2T_2^- \qquad (3)$$

electron Nernstian process. In dichloromethane solution the peak-to-peak separation is ≥200 mV (Table III). The heterogeneous electron-transfer rate is slower in dichloromethane than in acetonitrile. The formal potentials of couple 3 in the complexes in acetonitrile lie in the range 0.1–0.2 V. Thus, RuX_2T_2 is a relatively weak oxidant—weaker than RuT_3^+ (couple 1).

The chelates undergo a second one-electron (from current-height considerations) voltammetric reduction on the negative side of SCE (Table III), which is logically assignable to process 4. On scan reversal, only an ill-defined anodic

$$RuX_2T_2^- + e^- \rightarrow RuX_2T_2^{2-} \qquad (4)$$

response is observed, suggesting that the dianion in reaction 4 is unstable. This is not surprising since even $RuX_2T_2^-$ is not stable on a longer time scale though it is stable on the cyclic voltammetric time scale.

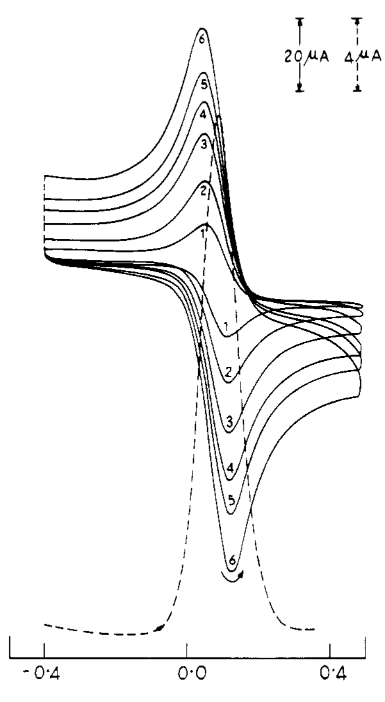

Figure 3. Voltammograms of $RuCl_2T_2$ (0.89 × 10^{-3} M) in CH_3CN (0.1 M TEAP) at a platinum working electrode: (—) cyclic voltammograms at scan rates of (1) 20, (2) 50, (3) 100, (4) 150, (5) 200, and (6) 300 mV s^{-1}; (---) differential-pulse voltammogram at scan rate 10 mV s^{-1} and modulation amplitude 25 mV.

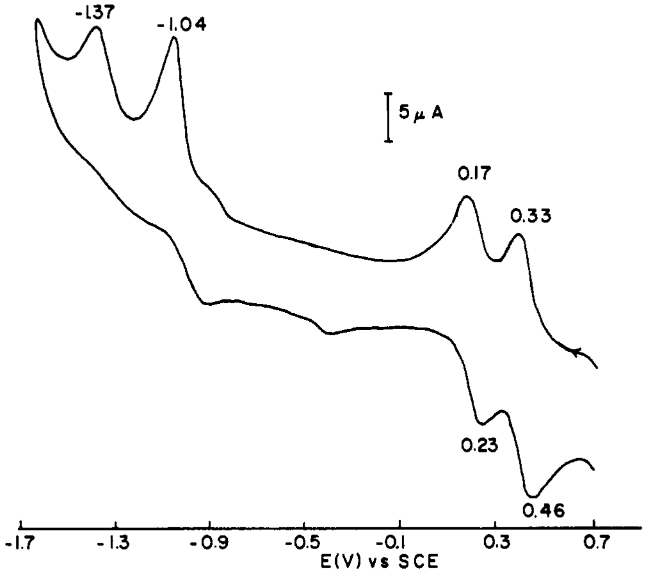

Figure 4. Cyclic voltammogram of a coulometrically reduced (−0.2 V) solution of **5** in CH_3CN at a platinum electrode (scan rate 50 mV s^{-1}).

Thus, coulometric reduction of RuX_2T_2 at a potential appropriate for the formation of $RuX_2T_2^-$, viz. −0.2 V vs. SCE, results in a species whose cyclic voltammogram is quite different from that of RuX_2T_2. A case is illustrated in Figure 4. Two equal and nearly reversible (peak-to-peak separation 60–80 mV) one-electron responses occur at positive potentials.[24] A reasonable explanation is that $RuX_2T_2^-$ dimerizes

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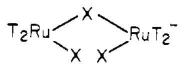
(24) The sum of the current heights (e.g. cathodic) of the two responses is found to be equal to the corresponding current height in couple 3 before electrolysis. Thus, 7.11 mg of **5** in 20 mL of MeCN gives a current height (couple 3) of 30 μA. After coulometric reduction at −0.20 V, each of the two peaks has the height of 15 μA.

via halide loss, yielding species **8** or **9**. The two responses can



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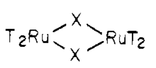

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then correspond to the two successive Ru(IV)–Ru(III) couples of the dimer. The two expected reductive responses (Ru(III) → Ru(II)) are seen on the negative side of SCE; the corresponding anodic responses are ill-defined. Further studies on the proposed dimers are in progress.

E. Concluding Remarks. The triazene 1-oxide frame is a relatively simple N,O type ligand that binds many metal ions in their common oxidation states.[18,19,23] Since ruthenium(IV) is usually considered to be a potent oxidant, the ready formation of octahedral RuX_2T_2, having normal chelate-ring parameters, and its stability are somewhat unexpected. The present results suggest that stable species of the type $Ru^{IV}X_2(bidentate)_2$ be obtainable from a variety of uncomplicated and common ligands.

The possible synthesis of RuX_2T_2 by the reaction of RuT_3 with X_2 was explored. The required complex is indeed formed in this way but only as a constitutent of a relatively complex mixture. Only in the case of X = I does the product approach the composition RuI_2T_2. However, the iodo complex dissociates in solution, and its spectra and other properties are different from those of the X = Cl and Br species. Further studies are in progress.

Experimental Section

Materials. The RuT_3 complexes were prepared as before.[18] The solvents, supporting electrolyte, and dinitrogen for electrochemical work were purified/prepared in the usual manner.[18] All other reagents and chemicals were of reagent grade and were used as supplied.

Measurements. Electronic spectra and IR spectra were measured on a Pye Unicam SP8-150 spectrometer and a Beckman IR-20A spectrometer, respectively. All electrochemical experiments were performed under pure and dry nitrogen by using a PAR 370-4 electrochemistry system as described elsewhere.[18] The working electrode is a Beckman Model 39273 inlay electrode in voltammetric measurements. For coulometry a platinum-wire-gauze electrode was used. All electrochemical data were collected at 298 K and are uncorrected for junction potential.

Preparation of Complexes. The dichloro complexes were prepared by using either concentrated HCl or gaseous HCl. The following preparations are representative of the use of the two reagents.

Dichlorobis(1-ethyl-3-phenyltriazene 1-oxidato)ruthenium(IV) (3). To a magnetically stirred green solution of 0.13 g (0.2 mmol) of tris(1-ethyl-3-phenyltriazene 1-oxidato)ruthenium(III) in 15 mL of benzene was added 0.5 mL of concentrated HCl dropwise. Stirring was continued for 3 h during which period benzene evaporated away. The residue was then washed thoroughly with water until free from acid. The mass was dried in vacuo over P_4O_{10} and then recrystallized from a 1:1 dichloromethane–hexane mixture. The dark-colored crystals collected by filtration weighted 80 mg (yield 80%).

Dichlorobis(1-methyl-3-phenyltriazene 1-oxidato)ruthenium(IV) (5). Through a magnetically stirred solution of 0.10 g (0.18 mmol) of tris(1-methyl-3-phenyltriazene 1-oxidato)ruthenium(III) in 15 mL of benzene was passed HCl gas for 1 min. The reaction mixture was treated as above. The pure complex was obtained in 75% yield.

Dibromobis(1-methyl-3-phenyltriazene 1-oxidato)ruthenium(IV) (6). The amounts of tris(1-methyl-3-phenyltraizene 1-oxidato)ruthenium(III) and benzene were the same as in the previous preparation. The procedure followed the preparation of $RuCl_2T_2$ described above, except that concentrated HCl was replaced by concentrated HBr. The yield of pure **6** was 60%.

Analytical data for all complexes are in Table II.

Preparation of Crystals of 2. Hexane (10 mL) was layered over a solution of 25 mg of **2** in 1 mL of pure dichloromethane. The system was allowed to evporate very slowly. Stout needle-shaped crystals, dark green-brown in color, deposited in a few days' time.

Table IV. Pertinent Information about Data Collection and Refinement

formula	$RuCl_2O_2N_6C_{18}H_{24}$
fw	528.4
space group	$P2_1/n$
a, Å	9.824 (4)
b, Å	17.059 (7)
c, Å	6.564 (3)
β, deg	99.57 (1)
V, Å^3	1084.7 (15)
Z	2
d_{calcd}, g/cm^3	1.62
cryst size, mm	0.4 × 0.4 × 0.5
μ(Cu Kα), cm^{-1}	85.41
data collcn instrument	Syntex P$\bar{1}$, 5 °C
radiation (λ, Å)	Cu Kα (1.541 84), graphite monochromated
scan method	ω–2θ
data collcn range	6–115° (2θ); $+h,+k,\pm l$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	1139
no. of parameters refined	181
R^a	0.055
$R_w{}^b$	0.080
quality-of-fit indicator^c	2.2
largest shift/esd, final cycle	0.37
abs corr	semiempirical (ψ scans)
abs cor range	56.82–99.10 (% transmissn)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Table V. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Ru(1)	0.000	0.000	0.000	2.47 (2)
Cl(1)	0.2122 (2)	0.0371 (1)	0.2035 (3)	3.82 (4)
O(1)	0.1037 (6)	−0.0219 (3)	−0.2268 (8)	3.3 (1)
N(1)	0.1688 (6)	−0.0892 (3)	−0.2028 (9)	3.0 (1)
N(2)	0.1488 (6)	−0.1380 (3)	−0.0610 (9)	3.0 (1)
N(3)	−0.0607 (6)	0.1114 (3)	−0.0544 (9)	2.8 (1)
C(1)	−0.0375 (7)	0.1663 (4)	−0.207 (1)	2.8 (1)
C(2)	−0.1140 (8)	0.2358 (4)	−0.244 (1)	3.4 (2)
C(3)	−0.0960 (8)	0.2830 (4)	−0.407 (1)	3.5 (2)
C(4)	−0.0048 (7)	0.2640 (5)	−0.540 (1)	3.1 (2)
C(5)	0.0700 (8)	0.1975 (5)	−0.497 (1)	3.7 (2)
C(6)	0.0582 (8)	0.1485 (4)	−0.334 (1)	3.6 (2)
C(7)	0.0108 (9)	0.3167 (5)	−0.719 (1)	4.2 (2)
C(8)	0.2707 (8)	−0.1038 (5)	−0.339 (1)	3.7 (2)
C(9)	0.3909 (8)	−0.0484 (6)	−0.293 (1)	4.4 (2)
H(2)	0.315 (8)	0.261 (5)	0.34 (1)	3 (2)*
H(3)	0.18 (1)	0.679 (6)	0.47 (1)	8 (3)*
H(5)	0.115 (5)	0.191 (3)	0.434 (8)	1 (1)*
H(6)	0.105 (6)	0.110 (3)	0.686 (8)	1 (1)*
H(7A)	0.449 (9)	0.790 (5)	0.33 (1)	6 (2)*
H(7B)	0.05 (1)	0.353 (7)	0.31 (2)	8 (3)*
H(7C)	0.418 (8)	0.159 (5)	0.71 (1)	5 (2)*
H(8A)	0.208 (6)	0.340 (3)	0.799 (9)	2 (1)*
H(8B)	0.224 (8)	0.907 (5)	0.53 (1)	5 (2)*
H(9A)	0.08 (1)	0.446 (7)	0.65 (2)	8 (3)*
H(9B)	0.447 (8)	0.941 (5)	0.62 (1)	5 (2)*
H(9C)	0.36 (1)	0.008 (4)	0.68 (1)	4 (2)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + (ab\cos\gamma)\beta(1,2) + (ac\cos\beta)\beta(1,3) + (bc\cos\alpha)\beta(2,3)]$.

X-ray Crystallographic Procedures. The structure of a single crystal was determined by applying the general procedures that we have already described elsewhere.[25] A detailed description is available as supplementary material. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table IV. Table V lists the atomic coordinates while

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(25) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. (c) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351. (d) Calculations were done on the PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX, with software from the Enraf-Nonius SDP-PLUS package.

Table I gives important bond distances and angles. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material. Figure 1 shows the structure and atom-numbering scheme.

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Registry No. **1** (R = Et, R′ = Me), 86502-52-5; **1** (R = Et, R′ = H), 86502-53-6; **1** (R = Et, R′ = Cl), 86502-54-7; **1** (R = Me, R′ = H), 89746-68-9; **2**, 89746-63-4; **3**, 89746-64-5; **4**, 89746-65-6; **5**, 89746-66-7; **6**, 89746-67-8; HCl, 7647-01-0; HBr, 10035-10-6.

Supplementary Material Available: Details of the X-ray procedures and tables of general temperature expressions, bond angles, bond distances, and observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

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Tridentate 1-Methyluracil in a Tetranuclear Pt_2,Ag_2 Complex. Crystal Structure and Solution Behavior of Bis(μ_3-1-methyluracilato)bis(*cis*-diammineplatinum(II))disilver Tetranitrate–2-Water (Head–Tail), *cis*-$[(NH_3)_2Pt(C_5H_5N_2O_2)Ag]_2(NO_3)_4\cdot 2H_2O$

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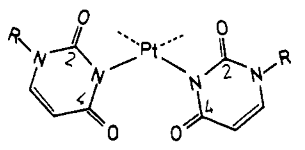
The interaction of a mono- and a dinuclear complex of *cis*-$(NH_3)_2Pt^{II}$ containing the 1-methyluracil anion ligand, 1-MeU, *cis*-$[(NH_3)_2Pt(1\text{-MeU})H_2O]^+$ (**1**) and *cis*-$[(NH_3)_2Pt(1\text{-MeU})]_2{}^{2+}$ (head–tail) (**2**), with $AgNO_3$ in aqueous solution has been studied by ^1H NMR spectroscopy, and two heteronuclear complexes containing Pt(II) and Ag(I) bound to 1-MeU have been isolated and characterized. The crystal structure of the head–tail Pt(II) dimer derivative has been determined. *cis*-$[(NH_3)_4Pt_2(C_5H_5N_2O_2)_2Ag_2](NO_3)_4\cdot 2H_2O$ crystallizes in the monoclinic space group $C2/c$ with 4 formula units in a cell having dimensions a = 13.810 (2) Å, b = 16.279 (2) Å, c = 11.871 (2) Å, and β = 95.58 (1)°. The structure has been refined on 1797 reflections to R = 0.051 and R_w = 0.056. The two ligands are arranged in head–tail fashion. Each 1-MeU ligand bridges two *cis*-$(NH_3)_2Pt^{II}$ through N(3) and O(4) and at the same time is bound to Ag through O(2). Thus, the 1-MeU ligands are tridentate, binding two Pt(II) and one Ag(I). The four heavy atoms are lined up within the molecular cation, giving rise to intramolecular distances of 2.892 (1) Å for Pt–Pt and 2.853 (2) Å for Pt–Ag. Adjacent cations are related by a C_2 symmetry operation, leading to an intermolecular Ag–Ag separation of 3.954 (3) Å, with nitrate ions bridging neighboring Ag atoms. The Pt coordination spheres show some deviation from pure square-planar toward a distorted tetrahedral geometry. The second heteronuclear complex that has been isolated is *cis*-$[(NH_3)_2(ONO_2)Pt(C_5H_5N_2O_2)Ag]NO_3$. It contains Pt(II) bound to the 1-MeU ligand through N(3) and Ag(I) coordinated through O(4) and/or O(2). IR and Raman spectra are used to support this interpretation, and the usefulness of vibrational spectroscopy for the study of heteronuclear $Pt_xAg_yL_z$ complexes is critically examined. ^1H NMR spectroscopy has been used to study the effect of Ag(I) on the equilibrium 2*cis*-$[(NH_3)_2Pt(1\text{-MeU})D_2O]^+ \rightleftharpoons [(NH_3)_2Pt(1\text{-MeU})]_2{}^{2+}$ (head–tail). The results indicate a competition between Ag(I) and Pt(II) for O(4) of 1-MeU, very much as in the system Ag(I)/*cis*-$[(NH_3)_2Pt(1\text{-MeU})]_2{}^{2+}$ (head–head).

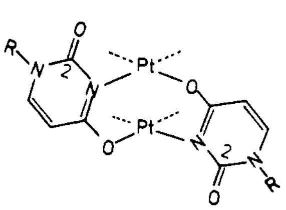
Introduction

In the course of our studies on the coordinating properties of the *cis*-diammineplatinum(II) residue toward the model nucleobases 1-methyluracil and 1-methylthymine and the interaction of the products formed with additional metal ions, we have thus far isolated and structurally characterized three types of heteronuclear complexes. These compounds are of Pt,M,L_2; Pt_2,M,L_4; and Pt_4,M,L_4 stoichiometries, with Pt representing *cis*-$(NH_3)_2Pt^{II}$, M the heterometal, and L the monoanion of 1-methyluracil, 1-MeU, and 1-methylthymine, 1-MeT, respectively (counterions omitted).[2-4] All three types of compounds (I) are derivatives of *cis*-$(NH_3)_2PtL_2$ and are obtained on subsequent reaction with a second *cis*-$(NH_3)_2Pt^{II}$ and/or other heterometal ions. Coordination of the second and third metal occurs stepwise, with occupation of the exocyclic oxygens of L taking place in pairs, e.g. O(4),O(4) and O(2),O(2). Formation of these heteronuclear complexes may be attributed to two factors: the favorable stereochemical arrangement of the four exocyclic oxygens for metal coordination and the increased basicities of these sites as a consequence of Pt(II) replacing the proton at N(3) of 1-methyluracil and 1-methylthymine.[3a,5]



I

The present study has been undertaken to separate these two factors by studying the ligating properties of the head–tail dimer *cis*-$[(NH_3)_2Pt(1\text{-MeU})]_2(NO_3)_2$ toward Ag(I). In this dimer (II), the structure of which has been reported by Faggiani et al.,[6] the only oxygens available for additional metal binding, O(2), are too far away to accommodate any joint intramolecular interaction for binding of a third metal ion. Consequently, any metal binding to these sites should be attributed essentially to the influence of the electron distribution in the N(3),O(4)-bridged 1-methyluracilato ligand.



II

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[1] On leave from the Sektion für Röntgen- und Elektronenbeugung, Universität Ulm, 79 Ulm, FRG.

[2] Neugebauer, D.; Lippert, B. *J. Am. Chem. Soc.* **1982**, *104*, 6596.

[3] (a) Lippert, B.; Neugebauer, D. *Inorg. Chim. Acta* **1980**, *46*, 171. (b) Lippert, B.; Schubert, U. *Ibid.* **1981**, *56*, 15.

[4] Lippert, B.; Neugebauer, D. *Inorg. Chem.* **1982**, *21*, 451.

[5] Lippert, B. *Inorg. Chim. Acta* **1981**, *55*, 5.

[6] Faggiani, R.; Lock, C. J. L.; Pollock, R. J.; Rosenberg, B.; Turner, G. *Inorg. Chem.* **1981**, *20*, 804.

0020-1669/84/1323-1713$01.50/0