Dibenzo[b,i]-1,4,8,11-tetraazacyclotetradecine Complexes. 3. Preparation and Molecular Structure of an Unprecedented Diruthenium(II) Compound, Ru₂(Htmtaa)(O₂CCH₃)₃(PhCCPh)

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Abstract: The unprecedented title compound, $Ru_2(C_{22}H_{23}N_4)(O_2CCH_3)_3(PhCCPh)$, where $C_{22}H_{23}N_4$ = Htmtaa, has been prepared and studied by X-ray crystallography, cyclic voltammetry, and several forms of spectroscopy. The compound is diamagnetic as determined by NMR. The structure of the molecule has two notable features: The two ruthenium atoms, 2.633 (1) Å from each other, are of unequal coordination number and only one tmtaa ligand is bonded to the "Ru₂" frame. The latter feature is of special interest since it presents the first example of a transition metal–tmtaa dimer in which the title ligand uses one of its four nitrogen atoms to bridge the metal centers. The title compound crystallizes as $Ru_2(C_{24}H_{23}N_4)(O_2CCH_3)_3(C_6H_5CCC_6H_5) \cdot C_{22}H_{24}N_4 \cdot C_7H_8$ in space group $P\bar{1}$ with a = 15.526 (5) Å, b = 16.869 (6) Å, c = 13.170 (5) Å, α = 103.76 (3)°, β = 108.98 (3)°, γ = 94.48 (3)°, V = 3122 (2) Å³, and Z = 2.

Introduction

The area of synthesis and structural characterization of transition-metal complexes containing the title macrocycle ligand, a dianion that is usually abbreviated tmtaa, continues to grow unabated.[1] The reason behind this high level of activity is 2-fold. (1) The ligand shares many common characteristics with porphyrins and thus allows us to use it as a model for biological phenomena. (2) The ligand's unique features with regard to electronic delocalization, core size, and framework flexibility dictate its own interesting reactivity and coordination geometry.[2] Although in the majority of the "M(tmtaa)"-type compounds this tetraaza[14]annulene ligand acts as a tetradentate dianionic unit (see diagram 1), there is a growing number of examples in which the ligand exhibits some different behavior.

H₂tmtaa   tmtaa²⁻   (1)
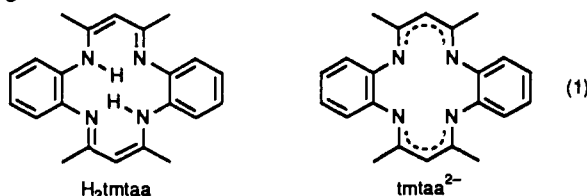
Novel behavior can be seen, for instance, in the Ru(tmtaa)-(PMePh₂)₂ complex,[3] where the usual saddle-shape conformation of the macrocycle is replaced by a "steplike" geometry. W-(CO)₄(tmtaa)[4,5] displays another anomaly. Here, the ligand maintains its neutrality by a proton shift upon coordination to the metal center and functions as a bidentate ligand. Finally, the dinuclear molecules of transition metals with tmtaa attract much attention in view of their stability despite the potential steric repulsions of the bulky, macrocyclic fragments.[6]

We report here the preparation and properties, including the structure, of Ru₂(Htmtaa)(O₂CCH₃)₃(PhCCPh), a complex that is unprecedented in its nature for the following reasons: (1) the novelty of having only one tmtaa ligand attached to the metal-metal bonded ruthenium dimer; (2) the unique way in which the macrocycle uses one of its four nitrogen atoms to bridge the two

ruthenium centers; 3) the unsymmetrical nature of the whole molecule stemming from the novel attachment of the acetylene moiety both to the tmtaa ligand and the "Ru₂" fragment.

Experimental Section

All manipulations were carried out under an argon atmosphere using standard vacuum-line and Schlenk techniques. All solvents were freshly distilled under nitrogen from the appropriate drying agents. Starting materials, Ru₂(O₂CCH₃)₄[7] and H₂tmtaa,[8] were prepared according to the literature. Diphenylacetylene was purchased from Aldrich.

Ru₂(Htmtaa)(O₂CCH₃)₃(PhCCPh). Method A. Ru₂(O₂CCH₃)₄, 0.05 g (0.11 mmol), H₂tmtaa, 0.08 g (0.22 mmol), and PhC≡CPh, 0.09 g (0.50 mmol), were suspended in 16 mL of toluene. The reaction mixture was brought to the point of reflux and maintained at reflux for 20 h. The final golden green solution was cooled to room temperature, filtered through Celite, and layered with 30 mL of hexanes. A plentiful crop of brown/yellow crystals deposited on the sides of the Schlenk tube in 48 h. The solution was then decanted and the crystals were vacuum dried, yield ca. 0.07 g (50%). This crystalline material contains interstitial H₂tmtaa and toluene (as shown by ¹H NMR and X-ray crystallography). ¹H NMR (C₆D₆): δ 1.29 (s,CH₃), 1.50 (s,CH₃), 1.61 (s,CH₃), 1.72 (s,CH₃), 1.81 (s,CH₃), 1.92 (s,CH₃), 2.06 (s,CH₃), 2.15 (s,CH₃), 4.71 (s,methine CH), 4.63 (d, methine CH), 6.69–8.20 (m, Ar protons), 13.16 (s, br, NH). UV–vis (C₆D₆ solution nm): λ 765 (w), 590 (b), 467 (sh), 347 (s). The crystalline product is relatively air-sensitive, undergoing decomposition within an hour of exposure to the atmosphere. It is moderately soluble in benzene, toluene, ethanol, and dichloromethane.

Method B. Ru₂(O₂CCH₃)₄Cl, 0.05 g (0.11 mmol), H₂tmtaa, 0.07 g (0.21 mmol), and PhC≡CPh, 0.09 g (0.50 mmol), were suspended in 16 mL of ethanol. The reaction mixture was brought to the point of reflux and maintained at reflux for 20 h. The final golden green solution was evaporated to dryness and the remaining solid was dissolved in 16 mL of dichloromethane. This solution was filtered through Celite and carefully layered with 20 mL of hexanes. After several days, large irregular crystals had formed on the bottom of the Schlenk tube. Unit cell dimensions were as follows (different from above): triclinic $P\bar{1}$ with a = 13.805 (4) Å, b = 15.017 (6) Å, c = 11.986 (2) Å, α = 108.05 (2)°, β = 103.26 (2)°, γ = 71.34 (2)°, and V = 2214 (1) Å³. These dimensions are different from the ones obtained in method A due to the absence of both free ligand and a toluene molecule in the asymmetric unit. In their place, two solvent molecules of dichloromethane were found. The Ru₂(Htmtaa)(O₂CCH₃)₃(PhCCPh) molecule is virtually identical in the two crystalline forms.

Measurements. The instruments were used as follows: Cary 17D, UV–vis; Varian XL-200E, ¹H NMR; BAS-100, cyclic voltammetry. Cyclic voltammograms were recorded at a Pt electrode with (n-Bu)₄NBF₄ solutions of CH₂Cl₂ as the electrolyte; the reference electrode was Ag/AgCl. Under the experimental conditions, ferrocene was oxidized at +0.54 V. The scan speed was 200 mV/s. All solutions used in

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Table I. Crystal Data for
$Ru_2(C_{22}H_{23}N_4)(O_2CCH_3)_3(C_6H_5CCC_6H_5)\cdot C_{22}H_{24}N_4\cdot C_7H_8$

formula	$Ru_2O_6N_8C_{71}H_{74}$
formula wt	1337.57
space group	$P\bar{1}$
a, Å	15.526 (5)
b, Å	16.869 (6)
c, Å	13.170 (5)
α, deg	103.76 (3)
β, deg	108.98 (3)
γ, deg	94.48 (3)
V, Å³	3122 (2)
Z	2
d_{calc}, g/cm³	1.423
cryst size, mm	0.46 × 0.40 × 0.15
μ(Mo Kα), cm⁻¹	5.313
data collecn instrument	AFC5R
radiatn monochromated in incident beam (Mo Kα, Å)	0.71073
orientatn reflcns, no., range (2θ)	23, 14.0 < 2θ ≤ 32.0
temp, °C	23 ± 1
scan method	2θ–ω
data collecn range, 2θ, deg	4 ≤ 2θ ≤ 46
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	8711, 6308
no. of params refined	784
transmission factors, max, min	1.00, 0.92
R^a	0.0479
R_w^b	0.0786
quality-of-fit indicator^c	1.855
largest shift/esd, final cycle	0.53
largest peak, e/Å³	0.75

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

the NMR and electrochemical measurements were prepared from the macrocrystalline material that appeared homogeneous by visual examination under a microscope.

X-ray Crystallography. Single crystals of $Ru_2(Htmtaa)(O_2CCH_3)_3$-(PhCCPh)·H_2tmtaa·C_7H_8 were grown by layering a toluene solution of the compound with hexanes. A rectangular brown/yellow crystal was selected from the product and was shown to be of good quality by polarized light microscopy. The crystal was coated with epoxy cement, mounted on a glass fiber, and put on the goniometer head of a Rigaku AFC5R diffractometer. Indexing revealed a triclinic cell, and the axial dimensions were confirmed with oscillation photographs. The data were collected with a constant speed of 4°/min in ω. Each scan was repeated four times or until $F/\sigma(F)$ reached 30, whichever came first. The data were collected to 46° in 2θ. Data were corrected for Lorentz and polarization effects[9] and absorption.[10] The empirical absorption correction made was based on ψ scans of several reflections with the Eulerian χ angle near 90°.
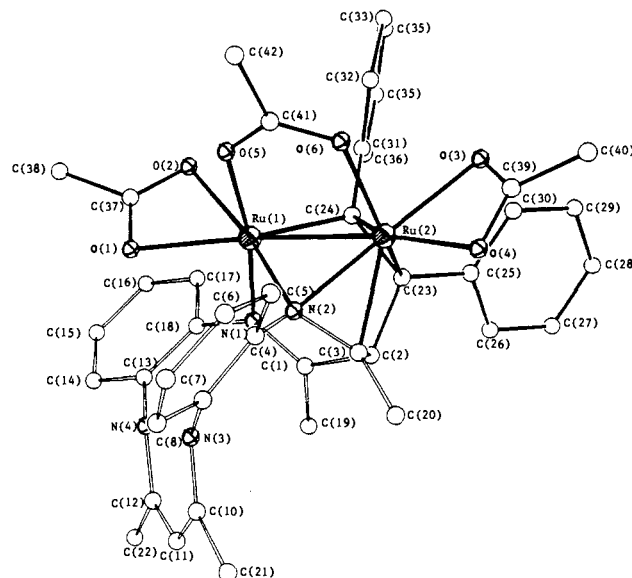
The heavy-atom positions were obtained via the first Patterson analysis. The subsequent development of the structure was done by an alternating sequence of least-squares refinements and difference Fourier maps. All atoms were treated anisotropically. One asymmetric unit contains the dinuclear molecule, a molecule of the tmtaa ligand in the neutral state and a toluene molecule, all in general positions. Crystallographic and procedural data are presented in Table I.

Results

Method of Preparation. The compound was prepared in good yield, as brown/yellow crystals, by the straightforward reaction of $Ru_2(O_2CCH_3)_4$ with H_2tmtaa and PhC≡CPh, see (2). It is

$$Ru_2(O_2CCH_3)_4 + 2C_{22}H_{24}N_4 + 2PhC\equiv CPh \rightarrow$$
$$Ru_2(C_{22}H_{23}N_4)(O_2CCH_3)_3(PhCCPh) +$$
$$C_{22}H_{24}N_4 + CH_3COOH \quad (2)$$

to be emphasized that this reaction is completely reproducible. The crystals contained an interstitial toluene molecule and H_2tmtaa, whose presence was confirmed by ¹H NMR.

Spectroscopic Results. The title compound gives a normal ¹H NMR (C_6D_6), confirming its diamagnetism. The general features of the NMR spectrum agree well with the crystal structure of the

(9) Calculations were done on a Local Area MicroVaxII (VAX/VMS V4.6) with the programs SHELX-86, SHELX-76, and the commercial package SDP.
(10) North, A. C. T.; Philips, D. C.; Matthews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

Figure 1. ORTEP diagram of the $Ru_2(Htmtaa)(O_2CCH_3)_3(PhCCPh)$ molecule, with the atom numbering scheme. All the atoms are represented by spheres of arbitrary size for clarity.

compound. First, the NMR spectrum of the crystals confirms the presence of the neutral ligand: 1.98 (s, 12 H), 4.78 (s, 2 H), 6.98 (m, 8 H), and 13.1 (s, 2 NH) ppm. Second, it displays the features of the main, dinuclear molecule with its highly asymmetric nature. There are all together eight different methyl groups present in the dimer and the toluene solvate molecule (four from the tmtaa ligand, three from acetate groups, and one from free toluene). Indeed, one can see eight singlets in the region between 1.29 and 2.15 ppm, with the toluene methyl group giving rise to a signal at 2.15 ppm. There are also two different methine protons in the bound macrocycle, C(11)–H and C(2)–H, and these are responsible for the two peaks at 4.71 ppm. The benzenoid rings of tmtaa, the phenyl groups of the PhC≡CPh moiety, and the toluene ring all give signals in the region 6.69–8.20 ppm. Lastly, three NH protons of the tmtaa ligands are found at 13.16 ppm.

The general features of the NMR spectrum agree well with the solid-state structure (vide infra) of the title compound. The assignment of the specific peaks of the spectrum to the specific methyl groups of the molecule is not possible because of the asymmetric nature of the molecule and the absence of couplings. We feel, however, that such an assignment is not of vital importance, since the geometry of the complex has been unequivocally established via X-ray crystallography, and the NMR spectrum shows clearly that this structure persists in solution.

Attempts to examine the electrochemical behavior of the compound by cyclic voltammetry were made. Unfortunately, the voltammogram seems to be dominated by the features of the free ligand present in the macrocrystalline material. The ligand shows a strong irreversible oxidation wave at +0.91 V, the region that coincides with the features of the title compound. The latter shows two irreversible oxidation waves at +0.99 and +1.32 V. We cannot say at this time whether these features are metal-related or they simply stem from the presence of the free ligand.

Structural Results—General Comments. The crystal structure was determined by standard procedures and afforded no special problems. To our surprise, an asymmetric unit contains not only the dinuclear molecule, but also a molecule of the tmtaa ligand in the neutral state, and a solvent molecule. The title molecule is shown in Figure 1, and its principal dimensions are listed in Table II.

As mentioned in the Introduction, this diruthenium molecule contains several striking features that deserve special attention. The two ruthenium atoms are 2.633 (1) Å from each other, suggesting a single bond. The metal atoms have different coordination numbers, with Ru(1) being seven-coordinate and Ru(2) having a coordination number of 8. There are three acetate groups

Table II. Selected Bond Distances (Å) and Bond Angles (deg) for $Ru_2(Htmtaa)(O_2CCH_3)_3(PhCCPh)$[a]

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Ru(1)	Ru(2)	2.633 (1)	Ru(2)	O(3)	2.134 (4)	N(1)	C(1)	1.281 (9)
Ru(1)	O(1)	2.165 (5)	Ru(2)	O(4)	2.198 (5)	N(2)	C(3)	1.400 (9)
Ru(1)	O(2)	2.161 (5)	Ru(2)	O(6)	2.173 (5)	C(1)	C(2)	1.488 (9)
Ru(1)	O(5)	2.085 (5)	Ru(2)	N(2)	2.036 (4)	C(2)	C(3)	1.558 (11)
Ru(1)	N(1)	2.066 (5)	Ru(2)	C(3)	2.089 (6)	C(2)	C(23)	1.538 (8)
Ru(1)	N(2)	2.010 (6)	Ru(2)	C(23)	2.186 (7)	C(23)	C(24)	1.450 (10)
Ru(1)	C(24)	2.023 (7)	Ru(2)	C(24)	2.025 (7)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Ru(2)	Ru(1)	O(1)	154.8 (2)	N(2)	Ru(1)	C(24)	90.9 (3)	O(6)	Ru(2)	C(3)	134.2 (3)
Ru(2)	Ru(1)	O(2)	136.9 (1)	Ru(1)	Ru(2)	O(3)	136.4 (2)	O(6)	Ru(2)	C(23)	148.9 (2)
Ru(2)	Ru(1)	O(5)	81.4 (1)	Ru(1)	Ru(2)	O(4)	160.0 (1)	O(6)	Ru(2)	C(24)	109.7 (3)
Ru(2)	Ru(1)	N(1)	107.8 (2)	Ru(1)	Ru(2)	O(6)	87.6 (1)	N(2)	Ru(2)	C(3)	39.6 (3)
Ru(2)	Ru(1)	N(2)	49.8 (1)	Ru(1)	Ru(2)	N(2)	49.0 (2)	N(2)	Ru(2)	C(23)	90.1 (2)
Ru(2)	Ru(1)	C(24)	49.5 (2)	Ru(1)	Ru(2)	C(3)	75.4 (2)	N(2)	Ru(2)	C(24)	90.0 (2)
O(1)	Ru(1)	O(2)	60.5 (2)	Ru(1)	Ru(2)	C(23)	75.4 (2)	C(3)	Ru(2)	C(23)	66.7 (3)
O(1)	Ru(1)	O(5)	84.6 (2)	Ru(1)	Ru(2)	C(24)	49.4 (2)	C(3)	Ru(2)	C(24)	91.0 (3)
O(1)	Ru(1)	N(1)	85.4 (2)	O(3)	Ru(2)	O(4)	60.0 (2)	C(23)	Ru(2)	C(24)	40.0 (3)
O(1)	Ru(1)	N(2)	110.7 (2)	O(3)	Ru(2)	O(6)	79.7 (2)	Ru(1)	N(1)	C(1)	120.7 (4)
O(1)	Ru(1)	C(24)	155.6 (3)	O(3)	Ru(2)	N(2)	173.6 (2)	Ru(1)	N(2)	Ru(2)	81.2 (2)
O(2)	Ru(1)	O(5)	82.2 (2)	O(3)	Ru(2)	C(3)	139.8 (2)	Ru(1)	N(2)	C(3)	116.7 (5)
O(2)	Ru(1)	N(1)	93.1 (2)	O(3)	Ru(2)	C(23)	94.7 (2)	Ru(2)	N(2)	C(3)	72.2 (3)
O(2)	Ru(1)	N(2)	170.3 (2)	O(3)	Ru(2)	C(24)	96.3 (2)	N(1)	C(1)	C(2)	118.3 (5)
O(2)	Ru(1)	C(24)	98.6 (3)	O(4)	Ru(2)	O(6)	84.8 (2)	C(1)	C(2)	C(3)	117.2 (6)
O(5)	Ru(1)	N(1)	170.0 (2)	O(4)	Ru(2)	N(2)	114.0 (2)	C(1)	C(2)	C(23)	110.7 (6)
O(5)	Ru(1)	N(2)	93.3 (2)	O(4)	Ru(2)	C(3)	96.8 (2)	C(3)	C(2)	C(23)	98.9 (5)
O(5)	Ru(1)	C(24)	106.0 (2)	O(4)	Ru(2)	C(23)	119.0 (2)	Ru(2)	C(3)	N(2)	68.1 (3)
N(1)	Ru(1)	N(2)	89.9 (2)	O(4)	Ru(2)	C(24)	150.4 (2)	N(2)	C(3)	C(2)	117.1 (6)
N(1)	Ru(1)	C(24)	83.4 (2)	O(6)	Ru(2)	N(2)	98.1 (2)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

remaining on the Ru_2 moiety, from the starting material of $Ru_2(O_2CCH_3)_4$. It is important to note, however, that only one of three is still a bridging acetate; two are now chelating with one at each metal center. Interestingly, the bond distance between Ru(1) and O(5) (of the bridging acetate) is 2.085 (5) Å, which is considerably shorter than the distance of 2.173 (5) Å between Ru(2) and O(6). That may be caused by the increased coordination number of Ru(2) and consequently greater steric crowding around it.

The attachment of the diphenylacetylene fragment to the tmtaa ligand creates a complicated tridentate ligand. C(2) of tmtaa is 1.538 (8) Å away from C(23) of the acetylene, indicating a carbon–carbon single bond between the two atoms. The two carbon atoms of diphenylacetylene, C(23) and C(24), are 1.45(1) Å from each other, a distance whose significance will be addressed in detail in the Discussion section; for now, it is important to point out the difference in environments about the two carbon atoms. C(23) serves as a bridge between Ru(2) and the activated methine carbon of tmtaa, C(2). On the other hand, C(24) bridges the two metal centers, Ru(1) and Ru(2), with an average Ru–C bond distance of 2.024 (7) Å.

The Macrocyclic Ligand. The unusual title complex contains a novel uninegative, tridentate tmtaa macrocycle that utilizes only two of its four nitrogen atoms, N(1) and N(2), in bonding to the Ru_2 frame. Basically, the ligand retains its usual saddle-shape conformation despite the novel coordination mode. The uncoordinated unit of N(3)–C(10)–C(11)–C(12)–N(4) consists of a planar imine–enamine double bond arrangement that is similar to the delocalization seen in the neutral ligand.[2] The other, bound end of the macrocycle behaves quite differently though. Due to the single bond between C(2) and C(23) of the diphenylacetylene unit, C(2) becomes an sp^3 hybridized carbon. Consequently, the coordinated fragment of tmtaa, consisting of N(1)–C(1)–C-(2)–C(3)–N(2), becomes nonplanar with two nitrogen–carbon double bonds, N(1)–C(1) and N(2)–C(3), and two carbon–carbon single bonds, C(1)–C(2) and C(2)–C(3). A notable feature of this arrangement is that the two nitrogen–carbon double bonds are not the same; indeed, the N(1)–C(1) bond is 1.281 (9) Å whereas the N(2)–C(3) is 1.400 (9) Å, which is quite a significant difference. The reason for the lengthening of the latter double bond is the strong interaction of its π-electrons with the metal

center. In turn, Ru(2) back-donates its electron density to the π^* orbitals of the double bond, adding to its elongation. This is, in fact, the first example of such η^2 bonding in a "M(tmtaa)"-type system.

The four carbon–nitrogen bonds of the o-phenylenediamine residues retain their predominant single bond character with bond distances in the range 1.415 (9)–1.47 (1) Å.

Finally, the bond distances and angles of the tmtaa ligand in the neutral state, H_2tmtaa, which is present in the same asymmetric unit, are consistent with the values published previously by Goedken and co-workers.[2] We shall not discuss them here in detail.

Discussion

This compound poses an interesting problem not only from the structural point of view, as was presented above, but also from the bonding standpoint. Two important questions need to be addressed before we can arrive at a bonding scheme for the molecule: (1) What is the charge on the bound tmtaa ligand and (2) what are the oxidation states of the ruthenium atoms?

The diamagnetism of the title compound clearly helps us in narrowing down the options. Even so, we see three possibilities, which deserve careful consideration. The three cases, Figure 2, have ruthenium valences of (+2, +2), (+3, +3), or (+4, +4). In the discussion that follows, we need only consider the bound fragment of the macrocyclic ligand, that of N(1)–C(1)–C(2)–C(3)–N(2), along with the Ru_2 and "PhC=CPh" moieties. In all three cases the three acetate groups are each assigned a negative charge. The "tmtaa-PhCCPh" fragment is formulated as uninegative, trinegative, or pentanegative (formally) in cases I, II, and III, respectively.

Case I. In this case, we consider the ruthenium atoms to be in the +2 oxidation state (or perhaps +1, +3 if we write the Ru–Ru bond as a dative one, Ru→Ru. Either way the negative charge of the tmtaa-PhCCPh unit together with three acetate groups leaves a charge of +4 on the Ru_2 core.

We look at the tmtaa fragment N(1)–C(1)–C(2)–C(3)–N(2) as consisting of two nitrogen–carbon double bonds, N(1)—C(1) and N(2)—C(3), and two carbon–carbon single bonds, C(1)—C(2) and C(2)—C(3). From the bonding point of view, lone pairs of the two nitrogen atoms, N(1) and N(2), are directed toward
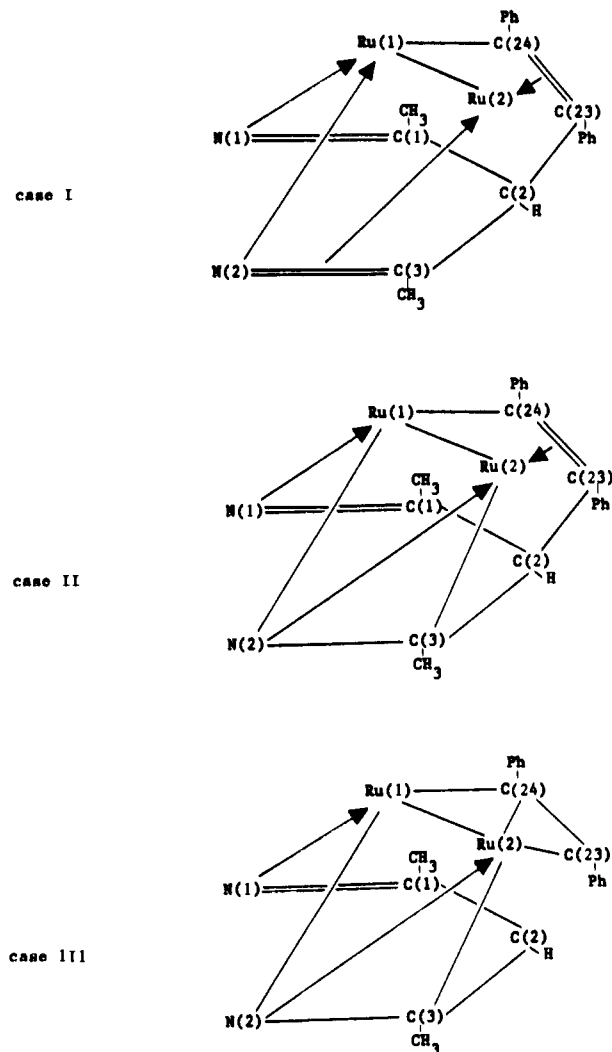
Figure 2. Schematic drawings depicting three possible ruthenium valences of (+2, +2), (+3, +3), or (+4, +4) for cases I, II, and III, respectively.

Figure 3. ORTEP diagram of the Ru(1)–C(24)–C(23)–Ru(2)–C(3)–N(2) cage, showing the highly symmetrical bonding environment about Ru(2).

Ru(1), with similar bond distances of 2.066 (5) and 2.010 (6) Å, respectively. On the other hand, Ru(2) accepts π-electron donation from the double bonds of N(2)=C(3) and C(23)=C(24), with 1.940 (5) and 1.970 (7) Å being the distances from Ru(2) to the center of each bond, respectively. The bonding environment about Ru(2), in this case, is highly symmetric. In fact, one could envision a mirror plane containing Ru(1), Ru(2), and C(2) to relate the following bonds to each other: N(2)=C(3) to C(23)=C(24) and C(1)—C(2) to C(2)—C(3). On that basis we can compare this fragment to a 1,4-pentadiene with two double bonds separated by two single bonds.

Case II. This case allows for the ruthenium atoms to be in the +3 oxidation state (or +2, +4). No longer do we consider the donation of π-electrons from the N(2)=C(3) double bond to Ru(2); instead, we create two two-center bonds, Ru(1)—N(2) and Ru(2)—C(3). Each bond has the negative charge localized on the nonmetal atom. On the other hand, N(2) is now donating its lone pair to Ru(2). In this formulation the symmetrical nature of the immediate bonding environment of Ru(2), evident in case I, has now been destroyed due to the formation of two new polar bonds, each adding a formal positive charge to the metal core and a formal negative charge to the ligand.

Case III. Here we carry over most features of case II but now we consider the bonding of the diphenylacetylene unit a little differently. In cases I and II, we presented one Ru(1)—C(24) bond at 2.023 (7) Å and a π-electron donation from the carbon–carbon double bond of the diphenylacetylene unit to the empty d orbital of Ru(2), as explained by the Dewar model.[11] One can,
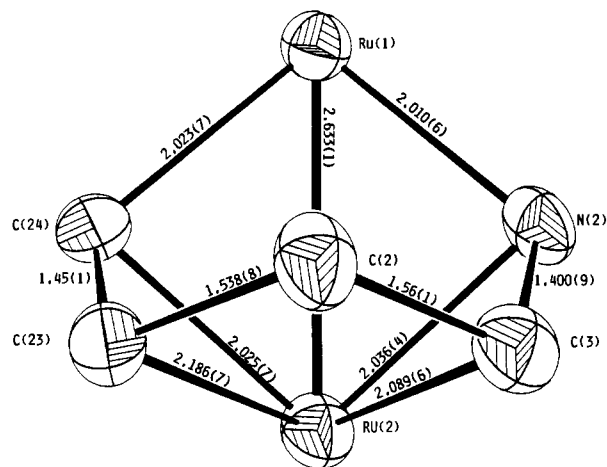
however, consider the PhCCPh unit as one forming two ruthenium–carbon bonds, Ru(2)—C(23) and Ru(2)—C(24). The five formal negative charges together with three acetate groups formally require the Ru$_2$ core to carry a +8 charge.

We believe that the title compound belongs to case I, with the ruthenium atoms in the +2 oxidation state. The reasons behind this confident assignment are 3-fold.

First, the bond distances of the bound fragment of tmtaa, N(1)–C(1)–C(2)–C(3)–N(2), point to the presence of two nitrogen–carbon double bonds, N(1)=C(1) and N(2)=C(3), which is true only for case I. The two distances are 1.281 (9) Å for N(1)—C(1) and 1.400 (9) Å for N(2)—C(3); it is apparent that the latter distance is longer than its counterpart. The difference can be explained by considering the back-donation of Ru(2) to the π* orbital of the N=C, which lengthens the bond. The bond distances of Ru(2) with N(2) and C(3) are virtually identical at 2.036 (4) and 2.089 (6) Å, respectively. The highly symmetrical bonding environment about Ru(2) can be seen in the ORTEP diagram of Figure 3. The imaginary mirror plane containing Ru(1), Ru(2), and C(2) "slices" the Ru(1)–C(24)–C(23)–Ru(2)–C-(3)–N(2) cage in half, relating four sets of distances to each other. Atoms N(2) and C(24) are not the same of course, but again the fragment of two double bonds, N(2)=C(2) and C(23)=C(24), separated by two single bonds resembles 1,4-pentadiene. The selected bond distances shown in the figure clearly support their equivalence.

Second, the bond distance of 1.45 (1) Å between C(23) and C(24) falls roughly in the range between a single and a double carbon–carbon bond. The π-electron donation of the diphenylacetylene unit to the empty d orbital of Ru(2) and the metal's back-donation to the π* orbital of the double bond would both have the effect of making the formally carbon–carbon double bond longer than expected. That effectively eliminates case III.

Third and last, the starting material in this reaction, Ru$_2$-(O$_2$CCH$_3$)$_4$, is a Ru(II,II) complex. The retention of the (+2, +2) valences throughout the reaction supports well the reaction scheme, shown in (2), of the Results section. The proposed reaction takes into account the presence of the neutral tmtaa ligand, which did not take part in the reaction. Indeed, the presence of this ligand was confirmed unequivocally by X-ray crystallography and ^{1}H NMR. The ruthenium atoms seem to remain in the +2 oxidation state throughout the reaction, with the loss of only one acetate group and a gain of a uninegative tmtaa-PhCCPh ligand.

It should be noted that while we propose that case I is the best single structure to represent the bonding, we also recognize that the electronic structure of this complex molecule can be viewed as a resonance hybrid to which I may be assigned merely the principal role but not an exclusive one, with II and perhaps even

(11) For background information on a Dewar model, see: Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980.

III making some contribution. The electron distribution featured in I is in accord with the concept of a cycloaddition or insertion of the PhC≡CPh molecule into the $Ru_2(Htmtaa)(O_2CCH_3)_3$ moiety. As a result, the diphenylacetylene group becomes a bridge between the methine carbon atom, C(2), of the tmtaa ligand and the two ruthenium atoms. This has much in common with an earlier report[12] of the addition of acetylene across the 2,4-pentanediiminato chelate ring and a cobalt atom in a mononuclear Co–tmtaa complex.

Concluding Remarks

In summary, the synthesis and characterization of the unprecedented title compound adds yet another example to the wide range of fascinating transition-metal complexes containing the dibenzo[*b,i*]-1,4,8,11 tetraazacyclotetradecine macrocyclic ligand. It can be concluded that the unique features of tmtaa, as listed in the Introduction, are the ones responsible for the continuing discoveries of a variety of new compounds.

In our ruthenium dimer, the macrocycle becomes a tridentate, uninegatively charged ligand, which for the first time uses one of its four nitrogen atoms to bridge two metal centers. In addition, the ruthenium dimer is a novel compound from the bonding point of view. It exhibits four η^2-type interactions between the Ru_2 core and the surrounding ligands as well as a metal–carbon bond that has the negative charge localized on the carbon.

The straightforward reaction of $Ru_2(O_2CCH_3)_4$, H_2tmtaa, and PhCCPh leads to a complex that, together with one one other example of a metal–metal bonded dimer containing one tmtaa ligand,[13] may lead the way to a new class of such compounds. Chemistry of this kind is currently under investigation.

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Regulation of Molecular Conformation of Chiral Tripodal Structures by Ca²⁺ Binding

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Abstract: Chiral ligands are introduced whose conformations may be regulated by the presence of Ca²⁺ ions. These compounds are assembled from two types of C_3-symmetric molecules as anchors (type 1 and type 2) and extended by chiral peptide residues. Their ion-binding properties are examined by a combination of experimental and theoretical tools (empirical force field (EFF) calculations). The calculations provide a conceptual framework in which to relate all the experimental observations into a coherent picture. The first type of compounds is shown to form complexes of prismatic geometry, inherently unfit to generate chiral complexes, while the second type forms complexes of octahedral coordination. Some of the ligands are found to generate Ca²⁺ complexes of optically active configurations and to thereby represent the first examples of chiral alkaline earth metal complexes. Ca²⁺ ions may thereby provide a viable exogenous means for the generation of chiral receptors from randomly arranged tripod-like molcules.

Introduction

Recently, we have introduced C_3-symmetric trispeptides that adopt propeller-like conformations of defined chiral sense by virtue of a belt of interstrand (or circular) H-bonds.[1] Extension of these trispeptides by ion binding groups such as catecholates[2] or hydroxamates[3], provided chiral receptors specific for ferric ions that mimic the properties of natural siderophores.[2,3] The absolute configuration of the resulting ferric complexes was found to be imposed by the chiral network of H-bonds in the receptor molecule.

However, the generation of chiral receptors from tripod-like molecules by H-bonds is generally limited to nonpolar solutions. In order to create chiral receptors also in polar media where H-bonds are broken, we aimed at generating tripod-like molecules whose conformation could be shaped by binding to alkali and alkaline earth metal ions as organizing elements. Such ion-induced intramolecular organization was envisioned to have the additional advantage of allowing exogenous control and regulation. Alkali and alkaline earth metal ions were conceived as eminently suitable for this task as they are characterized by fast-exchange kinetics. Among this family of metal ions, Ca²⁺ ions appeared to be particularly promising because of their high plasticity to fit various coordination geometries.[4,5] Extending such chiral ligands with binding cavities for ferric ions, for example, was anticipated to provide regulateable ferric ion carriers.

In this paper, we introduce tripod-like ligands (Figure 1) that form Ca²⁺ complexes of high chiral preference and thereby

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