CHEMISTRY LETTERS, pp. 1579-1580, 1989.

Asymmetrically Distorted Structure of (Polypyridyl)ruthenium(II) Complex with Sterically Hindered Ligand

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In $[Ru(phen)_2(dmphen)]^{2+}$(dmphen = 2,9-dimethyl-1,10-phenanthroline), the potential strong steric interaction between methyl groups and phen ligands was relieved not by the elongation of Ru-N (dmphen) bonds but by an asymmetrical distortion of coordination geometry. The phen ligands were compressed and the dmphen was elongated from the D_3 symmetry. The plane of dmphen tilted 15 from the N-Ru-N coordination plane.

In metal complexes with polypyridyl ligands α-hydrogen atoms of the ligand sometimes cause strong steric interaction with the neighboring polypyridyl ligands. Trans-$[Ru(N\text{-}N)_2L_2]$(N-N=2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen), L=monodentate ligand) has a distorted structure with twisted or bowed configurations (N-N=bpy), or tilt displacement (N-N=phen) to minimize the α-hydrogen interactions.$^{1)}$ Substitution of the α-hydrogen atoms for methyl groups in phenanthroline increases the steric interaction tremendously. Thus, the ligand 2,9-dimethyl-1,10-phenanthroline(dmphen), known as neocuproine, forms the tetrahedral bis complex specifically with Cu(I), making the two ligands twisted to each other to avoid the steric interaction. It does not form stable tris complex with first row transition metal ions. On the other hand, the ligand does form stable tris type complexes with Ru(II) and Os(II).$^{2)}$ In such a system it is interesting to know how the steric interaction of methyl groups with the neighboring ligands is relieved and what is the effect on the coordination geometry of the metal ion. In this letter the structure of a mixed ligand tris type Ru(II) complex, $[Ru(phen)_2(dmphen)](ClO_4)_2\cdot 0.5H_2O$, is reported in which novel distortions were found to relieve the steric interaction between the ligands.

The ruthenium(II) complex was synthesized for the first time from $[Ru(phen)_2Cl_2]$ and dmphen by refluxing them in ethanol-water (1:1) for 4 h. It was purified by SP-Sephadex chromatography and recrystallized from ethanol-water (1:1). The X-ray structural analysis was performed for the crystal.$^{3)}$

Figure 1 shows the structure of the complex ion projected along the pseudo C_3 axis and along the 'lost C_2 axis'. The Ru-N bond distance, and the two featuring angles are listed in Table 1 with those of $[Ru(bpy)_3]^{2+}$ $^{4)}$ and of the regular octahedron. Despite the methyl groups at 2 and 9 positions on dmphen or the potential steric interaction of them with the neighboring phen ligands, the Ru-

N(dmphen) bond distances showed quite normal value and were close to those of the unsubstituted phen. Instead, two types of unusual distortion that minimize the steric interactions were observed for the complex. First, the two phen ligands were compressed (larger Ψ values) and the dmphen was elongated (smaller Ψ value)5) from the D_3 symmetry and from the bpy ligands in $[Ru(bpy)_3]^{2+}$ (see Table 1).4) The "trigonally compressed-elongated" distortion is a new type of distortion to avoid steric interaction between ligands in complexes with a formula $[ML_2L']$(L,L'=bidentate ligand). As the second characteristics, the dmphen ligand plane had a specific angle (δ) with the coordination plane (N-Ru-N) of the ligand (Fig. 2 right), or Ru atom was outside the ligand plane. This tilt displacement breaks the 2-fold axis and makes the structure of the complex ion to be asymmetric as a whole. Similar situation, although less pronounced, was also observed for the phen ligands (see the δ values in Table 1). The distortion is of similar type as that observed for trans-$[Ru(phen)_2L_2]$ and known as tilt displacement,1) but is the first example for systems other than the trans complex. The tilt displacement can also be found in the reported structure of $[Fe(phen)_3]^{2+}$ although it was much less pronounced than that observed here.6) The structure found here indicated that Ru(II) prefers N_6 coordination even at the expense of big distortion from the regular octahedron. It also gives a good implication for a reaction intermediate of the monodentate phen ligand in the photosubstitution of $[Ru(phen)_3]^{2+}$.7)

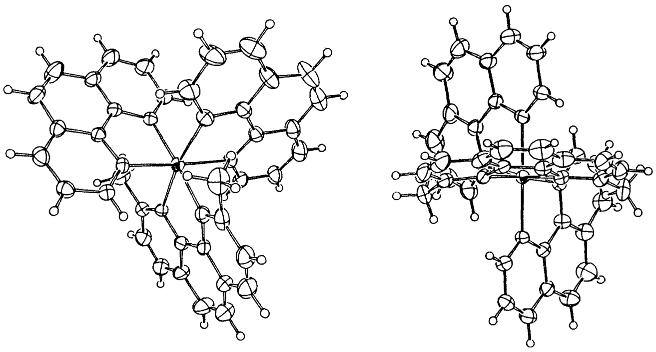

Fig. 1. Structure projected along pseudo C_3 axis and projected along bisection of N-Ru-N(dmphen).

Table 1. Geometrical parameters

Complex	Ru-N/Å	Ψ/° a)	δ/° b)
Octahedron	——	35.2	0.0
$[Ru(bpy)_3]^{2+}$ c)	2.06	33.5	0.0
$[Ru(L)_2(L')]^{2+}$ d)			
L =phen(1)	2.07	40.5	2.7
phen(2)	2.06	54.4	5.0
L'=dmphen	2.09	17.1	15.2

a) Dihedral angle between pseudo C_3 axis and N-Ru-N plane.
b) Dihedral angle between N-Ru-N plane and plane of the ligand.
c) $[Ru(bpy)_3](PF_6)_2$
d) $[Ru(phen)_2(dmphen)](ClO_4)_2 \cdot 0.5H_2O$

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3) $[Ru(phen)_2(dmphen)](ClO_4)_2 \cdot 0.5H_2O$: FW=868.7, monoclinic, $P2_1/n$, a=9.793(2), b=30.783(5), c=13.044(2)Å, β=110.00(1)°, V=3695(2)Å^3, Z=4, Dx=1.56 g cm^{-3}, μ(MoKα)=0.63 mm^{-1}. The Ru atom was located by Patterson function. Remaining non-H atoms were found by successive Fourier synthesese. Full-matrix least-squares anisotropically for all non-H atoms but ones of perchlorate gave R=0.074 for 4353 independent reflections ($4<2\theta<55°$) with $|Fo|>3\sigma(Fo)$.
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(Received June 15, 1989)