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Inorganica Chimica Acta 223 (1994) 177–179

Inorganica Chimica Acta

Note

Novel didentate 2,2′:6′,2″-terpyridine complexes of ruthenium(II)

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Received by Editor 24 February 1994; received by Publisher 14 April 1994

Abstract

The ruthenium(II) complex cations $[Ru(N,N',N''\text{-Xtpy})(N,N'\text{-Xtpy})Cl][PF_6]$ (Xtpy = 4′-substituted 2,2′:6′,2″-terpyridine) containing one didentate and one tridentate Xtpy ligand have been isolated as minor products from the synthesis of $[Ru(N,N',N''\text{-Xtpy})_2][PF_6]_2$.

Keywords: Ruthenium complexes; Polydentate ligand complexes; Terpyridine complexes

There have been numerous studies of $[Ru(N,N',N''\text{-Xtpy})_2]^{2+}$ (Xtpy = substituted 2,2′:6′,2″-terpyridine) and related complexes [1–3], and various synthetic methods have been used to obtain such complexes. In general, these complexes contain chelating tridentate tpy ligands. Although complexes containing didentate Xtpy ligands have been postulated for a number of years [4] it is only recently that this bonding mode has been unambiguously established [5,6]. We have described this as a hypodentate bonding mode [7]. In this note we report the isolation of products (**2**) containing didentate 2,2′:6′,2″-terpyridine ligands from the reaction of $[Ru^{III}(N,N',N''\text{-Xtpy})Cl_3]$ with Xtpy. These complexes with didentate ligands are significant side products in the 'normal' synthetic procedure for the preparation of $[Ru(N,N',N''\text{-Xtpy})_2]^{2+}$ salts. Such didentate species have attracted recent attention as intermediates for the formation of helicates and dendrimers [7].

The reaction of equimolar quantities of $[Ru(N,N',N''\text{-Xtpy})Cl_3]$ and Xtpy (X = H, Cl, MeO_2S) at reflux for 30 min in methanol in the presence of 4-ethylmorpholine or diethylamine as reductant yields a deep red–brown solution [1], from which orange $[Ru(N,N',N''\text{-Xtpy})_2][PF_6]_2$ (**3**) may be precipitated by the addition of $[NH_4][PF_6]$. This leaves a purple–brown solution in each case. Addition of water to this solution, followed by concentration in vacuo affords dark purple–brown precipitates, which were recrystallised from acetone–methanol to give $[Ru(N,N',N''\text{-Xtpy})(N,N'\text{-Xtpy})Cl][PF_6]$ (**2**) in 3–11% yield. Thin layer chromatography (silica; MeCN, sat. aq. KNO_3, H_2O, vol./vol. 7:1:0.5) showed that in some cases these products were contaminated with traces of $[Ru(N,N',N''\text{-Xtpy})_2][PF_6]_2$, which proved to be impossible to remove completely by column chromatography over silica utilising the same or different eluent systems. In each case, the mass spectrum (positive ion FAB) exhibited a molecular ion corresponding to $\{Ru(N,N',N''\text{-Xtpy})(N,N'\text{-Xtpy})Cl\}^+$, as well as a peak corresponding to loss of Cl. For example, $[Ru(N,N',N''\text{-MeO}_2\text{Stpy})(N,N'\text{-MeO}_2\text{Stpy})Cl][PF_6]$ exhibits such peaks at 759 (759) and 724 (724) (^{102}Ru and ^{35}Cl).

The ^1H NMR spectra (CD_3CN solution) of the didentate complexes **2** are consistent with the presence of one symmetrical tridentate Xtpy ligand, and one asymmetrical didentate Xtpy. The most notable features in each case are a doublet (1H) which is shifted downfield to $\approx \delta$ 10.2, and a doublet (1H) shifted upfield to $\approx \delta$ 6.2. The spectra are qualitatively very similar to that of [Ru(tpy)(pbpy)Cl][PF_6] (pbpy = 6-phenyl-2,2′-bipyridine), which has a similar pseudooctahedral N_5Cl donor set and which carries a non-coordinated phenyl ring of the didentate pbpy ligand in the position occupied by the non-coordinated ring of the Xtpy ligand in $[Ru(N,N',N''\text{-Xtpy})(N,N'\text{-Xtpy})Cl][PF_6]$ [8]. The ^1H NMR spectrum of $[Ru(N,N',N''\text{-Cltpy})(N,N'\text{-Cltpy})$-

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SSDI 0020-1693(94)03998-4

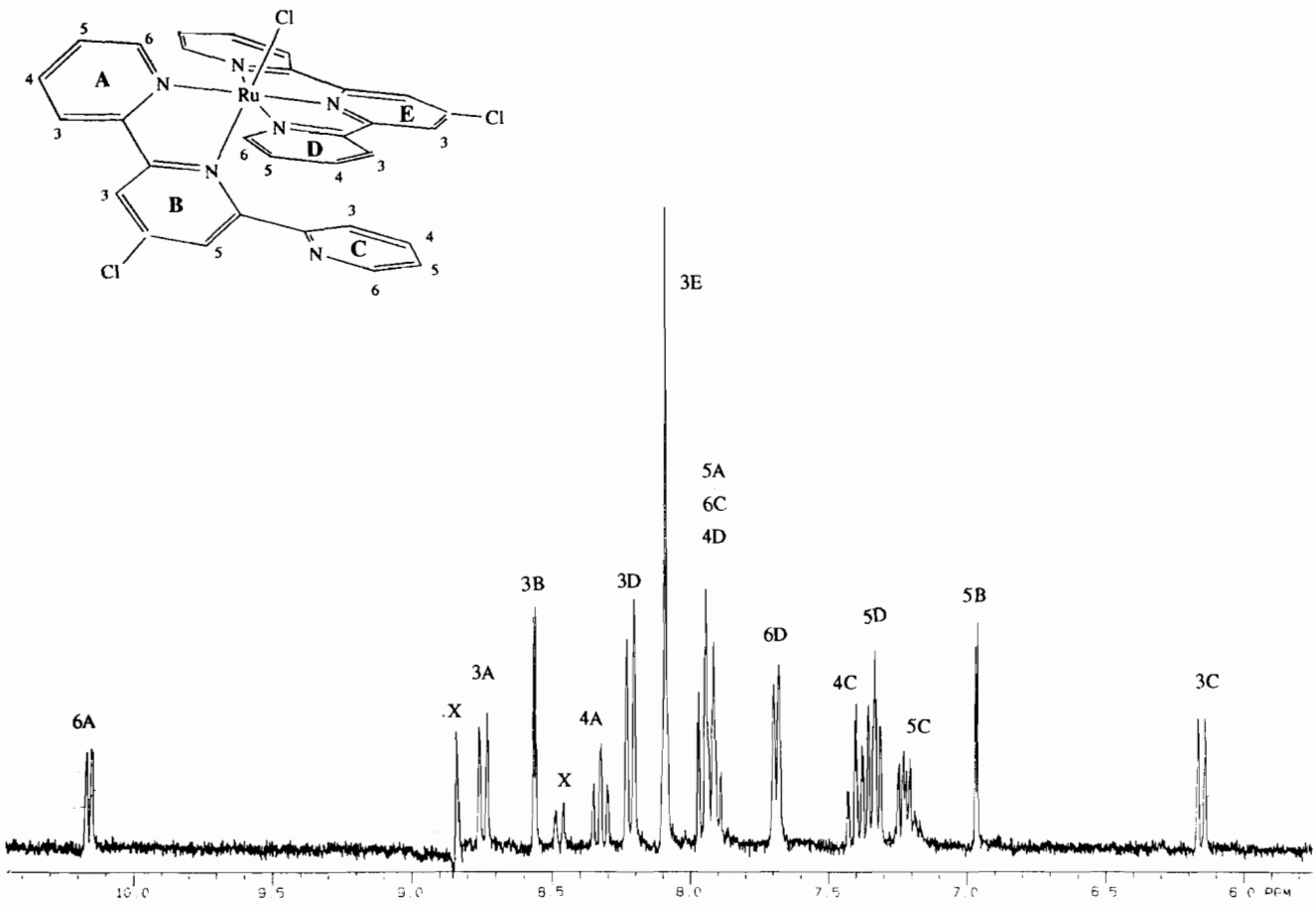
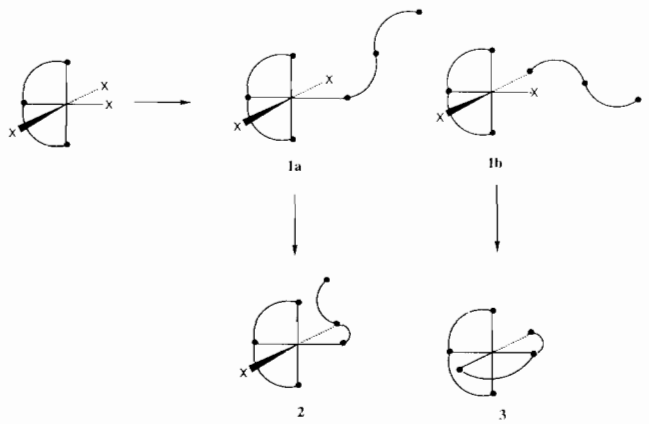


Fig. 1. ^{1}H NMR spectrum (300 MHz, CD_3CN) of [Ru(*N*,*N*′,*N*″-Cltpy)(*N*,*N*′,-Cltpy)Cl][PF_6]. Peaks marked X are due to a small impurity of [Ru(*N*,*N*′,*N*″-Cltpy)$_2$][PF_6]$_2$.



Scheme 1.

Cl][PF_6] (Fig. 1) was fully assigned by use of a 2D COSY experiment, as well as by comparison with that of [Ru(*N*,*N*′,*N*″-tpy)(*N*,*N*′-pbpy)Cl][PF_6] [8]. The doublet at δ 10.17 is assigned to H^{6A}, which is deshielded by the adjacent electronegative coordinated Cl. The peak at δ 6.15 corresponds to H^{3C} on the non-coordinated pyridine ring. This ring stacks with the tridentate tpy ligand, with the result that H^{3C} is shielded. These observations, along with the moderate stability of these complexes both in solution and in the solid state with respect to rearrangement to give **3**, are indicative of the didentate tpy being coordinated in such a way that the free pyridine ring is remote from, rather than adjacent to, the coordinated chlorine. The solution stability of the complex [Ru(*N*,*N*′,*N*″-Cltpy)(*N*,*N*′-Cltpy)Cl]$^+$ was studied. The complexes are thermally stable (heating for 72 h at 60 °C was required to completely convert a CD_3CN solution to [Ru(*N*,*N*′,*N*″-Cltpy)$_2$]$^{2+}$) but they are photolabile and photolysis (254 nm) of an identical solution resulted in $\approx$65% conversion to [Ru(*N*,*N*′,*N*″-Cltpy)$_2$]$^{2+}$ after only 15 min.

The main feature of the electronic spectra (MeCN solution) of the complexes is an intense metal-to-ligand charge transfer (MLCT) transition bathochromically shifted $\approx$30 nm with respect to that of the [Ru(*N*,*N*′,*N*″-Xtpy)$_2$][PF_6]$_2$ species. For example [Ru(*N*,*N*′,*N*″-MeO_2Stpy)(*N*,*N*′-MeO_2Stpy)Cl][PF_6] has λ_{max} 519 nm, ϵ 10 700 dm^3 mol^{-1} cm^{-1}, compared with λ_{max} 486 nm, ϵ 20 200 dm^3 mol^{-1} cm^{-1} for [Ru(*N*,*N*′,*N*″-MeO_2Stpy)$_2$][PF_6]$_2$. This bathochromic shift results in the complexes exhibiting purple–brown colours in MeCN

solution, compared to the orange–brown colours of $[Ru(N,N',N''\text{-Xtpy})_2][PF_6]_2$.

We believe that the formation and stability of these complexes follows from the sequential formation of M–N bonds with the tpy ligand. Consider the reaction of $[Ru(N,N',N''\text{-Xtpy})Cl_3]$ with Xtpy. The first new M–N bond will involve the terminal ring of the incoming ligand; this could be bonded *trans* (**1a**) or *cis* (**1b**) to the central ring of the tridentate Xtpy. Intermediate **1b** leads naturally to the $[Ru(N,N',N''\text{-Xtpy})_2]^{2+}$ species, whilst with non-labile metal centres **1a** leads to a didentate ligand and complex **2** (Scheme 1). As expected, **2**, is photolabile, but thermally stable.

We are currently extending these studies to related ligand systems.

Acknowledgements

We thank the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung (Grant No. 21-37325.93) for support.

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