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Thermal and Photo Control of the Linkage Isomerism of Bis(thiocyanato)(2,2′-bipyridine)platinum(II)

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Three linkage isomers, bis(thiocyanato-*S*)(2,2′-bipyridine)platinum(II) ([Pt(SCN)$_2$(bpy)]), (thiocyanato-*S*)(thiocyanato-*N*)(2,2′-bipyridine)platinum(II) ([Pt(SCN)(NCS)(bpy)]), and bis(thiocyanato-*N*)(2,2′-bipyridine)platinum(II) ([Pt(NCS)$_2$(bpy)]) were isolated, and their structures were elucidated. The crystal data are as follows: for [Pt(SCN)$_2$(bpy)], $C_{12}H_8N_4S_2Pt$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 12.929(9)$ Å, $b = 18.67(1)$ Å, $c = 5.497(4)$ Å, $Z = 4$; for [Pt(SCN)(NCS)(bpy)], $C_{12}H_8N_4S_2Pt$, monoclinic, $P2_1/n$ (No. 14), $a = 10.909(7)$ Å, $b = 7.622(4)$ Å, $c = 16.02(1)$ Å, $\beta = 102.323(7)°$, $Z = 4$; for [Pt(NCS)$_2$(bpy)], $C_{12}H_8N_4S_2Pt$, orthorhombic, *Pbcm* (No. 57), $a = 10.3233(8)$ Å, $b = 19.973(2)$ Å, $c = 6.4540(5)$ Å, $Z = 4$. The stacking structures of the isomers were found to be different depending on the coordination geometries based on the N- and S-coordination of the thiocyanato ligands, which control the color and luminescence of the crystals sensitively. The isomerization behaviors of the complex have been investigated both in solution and in the solid state. In solution, stepwise thermal isomerization from [Pt(SCN)$_2$(bpy)] to [Pt(NCS)$_2$(bpy)] by way of [Pt(SCN)(NCS)(bpy)] was observed using ^{1}H NMR spectroscopy. Reverse isomerization, from [Pt(NCS)$_2$(bpy)] to [Pt(SCN)(NCS)(bpy)] and [Pt(SCN)$_2$(bpy)], occurred when irradiated with near ultraviolet (UV) light. In contrast, the [Pt(SCN)$_2$(bpy)] yellow crystals exhibited thermal isomerization directly to red crystals of [Pt(NCS)$_2$(bpy)], as detected by changes in the emission spectrum, which indicates that the flip of two SCN$^-$ ligands correlatively occurred in the solid state. The yellow crystals of [Pt(SCN)(NCS)(bpy)] were also converted to the thermodynamically stable red crystal of [Pt(NCS)$_2$(bpy)] though the reverse isomerization has never been observed to occur by photoirradiation in the solid state.

Introduction

Linkage isomerism has been one of the more interesting and significant phenomena observed in coordination chemistry.[1] The thiocyanate ion is a typical ambidentate ligand, as is well-known. Generally speaking, the softness or hardness of metal ions dictate which form, the S-coordinated (M−SCN) or the N-coordinated (M−NCS), is favored more. Recently, (polypyridine)ruthenium(II) complexes containing N-coordinated thiocyanato ligands, *cis*-[Ru(NCS)$_2$(L)$_2$] (L = 2,2′-bipyridine (bpy) and its derivatives such as 4,4′-dicarboxy-2,2′-bipyridine), have attracted significant attention due to their high efficiency as dye sensitizers in solar cells.[2] The mixing of the S-coordinated forms, which are produced as a byproduct of the N-coordinated form or as a photoproduct during the photochemical processes, is a serious problem affecting efficiency, since the thiocyanate ligands play an important role in the control of the redox process.[3−5] Thus, control of linkage isomerization could be an important factor for their use as photosensitizers.

Several studies on the linkage isomerism of the thiocyanato ligand have been conducted for bis(thiocyanato)(α-diimine)platinum(II) complexes, [Pt(SCN)$_2$(L)] (L = bpy or substituted bpy).[6−9] For these types of complexes, three linkage

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(1) Burmeister, J. L. *Coord. Chem. Rev.* **1990**, *105*, 77−133.
(2) Hagfeldt, A.; Grätzel, M. *Acc. Chem. Res.* **2000**, *33*, 269−277.
(3) Kohle, O.; Ruile, S.; Grätzel, M. *Inorg. Chem.* **1996**, *35*, 4779−4787.
(4) Nazeeruddin, M. K.; Zakeeruddin, S. M.; Humphry-Baker, R.; Jirousek, M.; Liska, P.; Valchopoulos, N.; Shklover, V.; Fishcher, C.-H.; Grätzel, M. *Inorg. Chem.* **1999**, *38*, 6298−6305.
(5) Rensmo, H.; Södergren, S.; Patthey, L.; Westermark, K.; Vayssueres, L.; Kohle, O.; Brühwiler, P. A.; Hagfeldt, A.; Siegbahn, H. *Chem. Phys. Lett.* **1997**, *274*, 51−57.
(6) Kukushukin, Y. N.; Vrublevskaya, L. V.; Vlasova, R. A.; Isachkina, T. S.; Postnikova, E. S.; Sheleshkova, N. K. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1985**, *30*, 224−227.
(7) Coyer, M. J.; Croft, M.; Chen, J.; Herber, R. H. *Inorg. Chem.* **1992**, *31*, 1752−1757.

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isomers, M−(SCN)$_2$, M−(SCN)(NCS), and M−(NCS)$_2$, are expected, excluding the bridging types of the thiocyanato ligands. Coyer et al. have earlier reported the isolation and characterization of three linkage isomers for [Pt(SCN)$_2$(dmbpy)] (dmbpy = 4,4′-dimethyl-2,2′-bipyridine) using various spectroscopic techniques such as IR, NMR, and EXAFS.[8] For the simple bipyridine complex, however, only two linkage isomers, [Pt(SCN)$_2$(bpy)] and [Pt(NCS)$_2$(bpy)], were reported, and the existence of the third isomer, [Pt(SCN)(NCS)(bpy)], has never been identified.[7] The linkage isomerization of these platinum(II) complexes is characteristic in their remarkable color change in the solid state. This color change is related to the crystal structure, wherein the intermolecular Pt···Pt interactions are an important factor for coloration and luminescence, as is well-known for several (polypyridine)platinum(II) complexes.[10] Among bis(thiocyanato)(α-diimine)platinum(II) complexes, however, the only crystal structure reported thus far has been for a low quality red form of [Pt(NCS)$_2$(bpy)], which was shown to have a columnar stack with a short Pt···Pt distance of 3.34 Å.[10]

In this paper, we report the successful isolation and determination of the structures of all three linkage isomers for [Pt(SCN)$_2$(bpy)]. This is the first reported instance of complete structural determination of all three linkage isomers for bis-thiocyanato type complexes. We have also investigated isomerization behavior among these linkage isomers in the solid state and in solution, using luminescence and NMR spectroscopy, respectively.

Experimental Section

Synthesis and Separation of the Linkage Isomers. [PtCl$_2$(bpy)] was prepared according to a previous report in the literature.[11] The yellow product of [Pt(SCN)$_2$(bpy)] was synthesized by a method similar to that reported by Coyer et al.[7] To a DMSO solution of [PtCl$_2$(bpy)] (0.086 g, 0.2 mmol) was added an aqueous solution containing 2 equiv of AgNO$_3$ (0.068 g) and the reaction mixture stirred at 100 °C for 2 h. A gray precipitate of AgCl was removed by filtration. To the resulting yellow filtrate was added an aqueous solution of excess KSCN (0.104 g, 1 mmol) at ca. 5 °C resulting in the immediate formation of the yellow precipitate. The yellow precipitate was filtered and repeatedly washed with water to completely remove all traces of DMSO. This process of washing is very important to avoid the conversion of the yellow crystals to the red ones. The yellow crystals thus obtained were confirmed to be mostly [Pt(SCN)$_2$(bpy)] on the basis of ^{1}H NMR spectral data (described below). Yield: 0.082 g (90%).

Recrystallization of the yellow product from acetone, acetone/DMSO (99/1 v/v), and DMF formed yellow crystals of [Pt(SCN)$_2$(bpy)], yellow crystals of [Pt(SCN)(NCS)(bpy)], and red crystals of [Pt(NCS)$_2$(bpy)], respectively. ^{1}H NMR (300 MHz, DMSO-d_6, δ): for [Pt(SCN)$_2$(bpy)], 7.99 (t, 1H), 8.51 (t, 1H), 8.75 (d, 1H), 9.37 (d, 1H); for [Pt(SCN)(NCS)(bpy)], 7.86 (t, 1H), 8.03 (t, 1H), 8.45 (t, 1H), 8.53 (t, 1H), 8.67 (d, 1H), 8.73 (d, 1H), 8.80 (d, 1H), 9.08 (d, 1H); for [Pt(NCS)$_2$(bpy)], 7.92 (t, 1H), 8.49 (t, 1H), 8.64 (d, 1H), 8.73 (d, 1H). IR (KBr, cm^{-1}): ν(SC*N*) for [Pt(SCN)$_2$(bpy)], 2131, 2116; for [Pt(SCN)(NCS)(bpy)], 2132, 2107, for [Pt(NCS)$_2$(bpy)], 2117.

Table 1. Crystallographic Data for the Three Linkage Isomers

	[Pt(SCN)$_2$(bpy)]	[Pt(SCN)(NCS)(bpy)]	[Pt(NCS)$_2$(bpy)]
chemical formula	$C_{12}H_8N_4S_2Pt$	$C_{12}H_8N_4S_2Pt$	$C_{12}H_8N_4S_2Pt$
fw	467.43	467.43	467.43
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)	*Pbcm* (No. 57)
a/Å	12.929(9)	10.909(7)	10.3233(8)
b/Å	18.67(1)	7.622(4)	19.973(2)
c/Å	5.497(4)	16.02(1)	6.4540(5)
β/deg	90	102.323(7)	90
V/Å^3	1326(1)	1301(1)	1330.8(2)
Z	4	4	4
T/°C	−100	−100	−100
λ/Å	0.71073	0.71073	0.71073
D_{calcd}/g cm^{-3}	2.340	2.386	2.333
μ/cm^{-1}	108.38	110.51	108.04
R_1 (F_o)[a]	0.061	0.038	0.036
R_w (F_o^2)[b]	0.149	0.084	0.068
weighting scheme[b] x, y	0.0, 13.0379	0.0342, 3.6723	0.0002, 8.5977

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o)^2]^{1/2}$, $w = [\sigma_c^2(F_o^2) + (xP)^2 + yP]^{-1}$, $P = (F_o^2 - 2F_c^2)/3$.

Spectroscopic Measurements. Absorption spectra were measured on a Shimadzu UV-2500PC spectrometer. Emission spectra were obtained using a Shimadzu RF-5300PC equipped with a red-sensitive photomultiplier, Hamamatsu R928, without further correction with respect to the sensitivity of the detector. Time-resolved measurements for the emission lifetimes were performed with a Hamamatsu CF4780 system. The low-temperature measurements at 77 K were carried out using a liquid nitrogen Dewar or an Oxford DN1704 cryostat. ^{1}H NMR spectra were measured on a Varian Gemini 2000 spectrometer (300 MHz), and IR spectra were obtained on a JASCO FT/IR8900μ.

X-ray Crystallography. All X-ray diffraction data were collected on a Rigaku AFC-8/Mercury CCD system. Only the rough structure of [Pt(NCS)$_2$(bpy)] with isotropic thermal parameters for most non-hydrogen atoms has been reported previously.[10] We have determined this structure again, in addition to the structures of the other isomers, [Pt(SCN)$_2$(bpy)] and [Pt(SCN)(NCS)(bpy)]. All three structures were solved by a Patterson method[12] or a direct method,[13] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included and refined using a riding model.[14] The crystallographic data and final *R* indices are summarized in Table 1. All calculations were carried out using teXsan.[15]

Isomerization Experiments. Thermal isomerization of the linkage isomers in solution was pursued by means of ^{1}H NMR spectroscopy using a DMSO-d_6 solution at 25 °C. The thermal isomerization of the crystals was performed on a heating block maintained at 75 °C. For both solution and crystals, photoirradiation with near UV and vis light was carried out in an isothermal bath

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(8) Coyer, M. J.; Herber, R. H.; Chen, J.; Croft, M.; Szu, S. P. *Inorg. Chem.* **1994**, *33*, 716−721.

(9) Burmeister, J. L.; Basolo, F. *Inorg. Chem.* **1964**, *3*, 1587−1593.

(10) Connick, W. B.; Marsh, R. E.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1997**, *36*, 913−922.

(11) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1934**, 965−971.

(12) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Gould, R. O.; Smits, J. M. M. *PATTY*; Technical Report of the Crystallography Laboratory; University of Nijmegen: Nijmegen, The Netherlands, 1994.

(13) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR92. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(14) Sheldrick, G. M. *SHELXL-97*; University of Göttingen, Germany, 1997.

(15) *teXsan*; Molecular Structure Co., and Rigaku Co.: The Woodlands, TX, and Tokyo, Japan, 2000.

(25 °C) with a UV or vis band-pass filter (UV-D33 or V-42) by using an Ushio Optical Modulex SX-U1500SQ (500 W Xe lamp).

Results and Discussion

Isolation of Three Linkage Isomers. The addition of an aqueous solution of potassium thiocyanate to the reaction solution of [$PtCl_2$(bpy)] with silver nitrate in DMSO immediately produced the yellow precipitate, as described in the Experimental Section. When the reaction was performed at 5 °C, the product was primarily the single isomer of [$Pt(SCN)_2$(bpy)]. However, when the reaction was done at room temperature, the resulting yellow precipitate contained a small amount of [Pt(SCN)(NCS)(bpy)]. The products were easily identified by ^1H NMR measurements in acetone-d_6 because isomerization is very slow in acetone. Careful washing of the crystals with water is very important to prevent unexpected isomerization of the crystals.

Three linkage isomers were successfully isolated by recrystallization from different conditions. Pale-yellow prismatic crystals of [$Pt(SCN)_2$(bpy)] were produced from an acetone solution, and pale-yellow needle crystals of [Pt(SCN)(NCS)(bpy)] were obtained by using acetone/DMSO (99/1 v/v) as a recrystallization solvent at room temperature. The crystallization of these two crystals was accomplished very successfully in a bright room rather than under dark conditions. Light was found to be effective in the suppression of the isomerization of [$Pt(SCN)_2$(bpy)] and [Pt(SCN)(NCS)(bpy)] to [$Pt(NCS)_2$(bpy)]. Recrystallization from DMF under dark conditions in the absence of light yielded red needle crystals of [$Pt(NCS)_2$(bpy)]. The crystallization conditions for each isomer are related to the isomerization behavior, as described in a later section.

IR spectra of these isomers exhibited strong CN stretching bands, characteristic of the SCN^- ligands. The data for [$Pt(SCN)_2$(bpy)] and [$Pt(NCS)_2$(bpy)] are consistent with previously reported values.[7] However, it is difficult to distinguish the third isomer, [Pt(SCN)(NCS)(bpy)], from the others with certainty using IR data.

Structural Characteristics of Three Linkage Isomers. Figure 1 shows the molecular structures of the three linkage isomers, [$Pt(SCN)_2$(bpy)], [Pt(SCN)(NCS)(bpy)], and [$Pt(NCS)_2$(bpy)], and Table 2 lists selected bond lengths and angles for these complexes. The differences between S- and N-coordination are clear on the basis of the coordination bond lengths and angles. The S-coordination bonds are long (~2.3 Å) compared to the N-coordination bond lengths (~2.0 Å), and Pt−SCN is bent at 102−108°, whereas Pt−NCS shows a relatively linear geometry. Similar geometrical characteristics for the linkage isomers have also been reported for the palladium(II) complexes, bis(thiocyanato){bis(diphenylphosphine)alkyl or aryl}palladium(II) complexes,[16] and a mono thiocyanato complex, [$Pd(Et_2dien)(SCN)]^+$ (Et_2dien = 1,1,7,7-tetraethyldiethylenetriamine).[17] These features are reasonable considering the differences in the electronic structures of the N and S atoms. As a result, the structures of the three isomers for bis(thiocyanato)(2,2′-bipyridine)platinum(II) are quite different from each other.

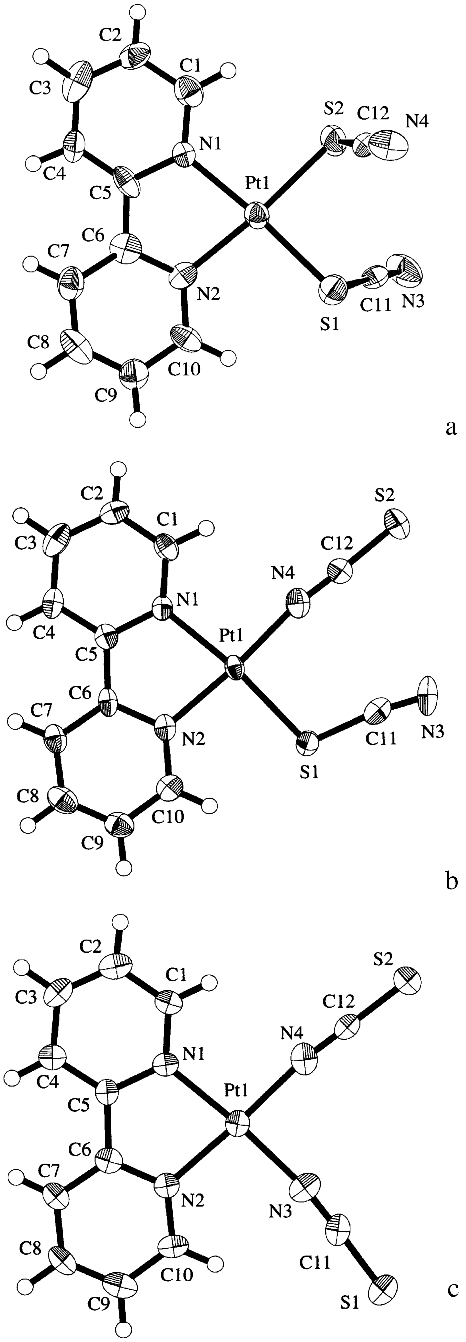

Figure 1. Molecular structures of the three isomers showing the numbering scheme: (a) [$Pt(SCN)_2$(bpy)], (b) [Pt(SCN)(NCS)(bpy)], and (c) [$Pt(NCS)_2$(bpy)].

It is interesting to note that [$Pt(SCN)_2$(bpy)] shows a chiral crystal structure, where two SCN^- ligands are directed up and down from the coordination plane, respectively. For [Pt(SCN)(NCS)(bpy)], however, the SCN^- ligand is almost in the coordination plane, oriented along the adjacent NCS^- ligand. This geometry is likely based on the most compact crystal packing rather than the steric constraint of the other ligand, which was pointed out for the above-mentioned palladium(II) complexes.[16] [$Pt(NCS)_2$(bpy)] has a completely

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(16) Paviglianiti, A. J.; Minn, D. J.; Fultz, W. C.; Burmeister, J. L. *Inorg. Chim. Acta* **1989**, *159*, 65−82.

(17) Brock, C. P.; Huckaby, J. L.; Attig, T. G. *Acta Crystallogr.* **1984**, *B40*, 595−606.

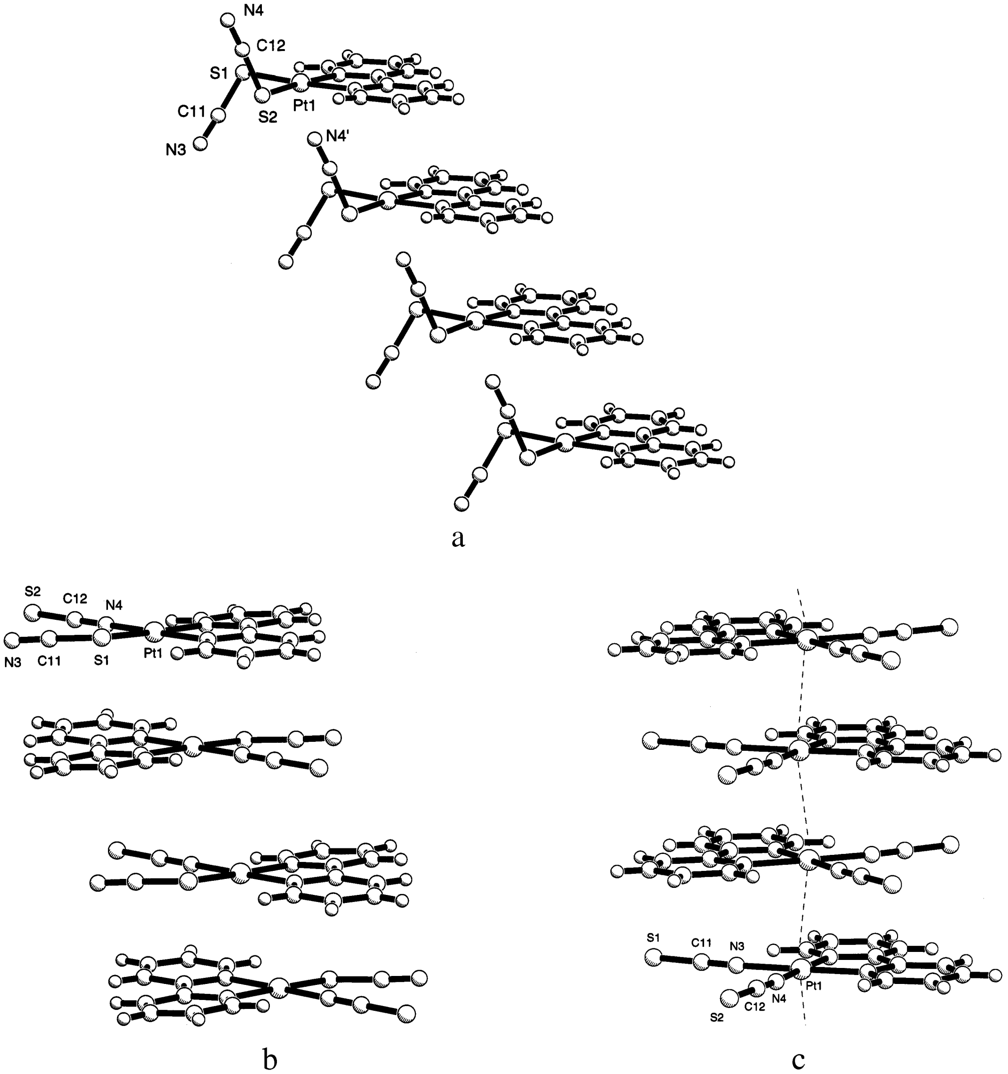

Figure 2. Stacking structures of the three isomers: (a) [Pt(SCN)$_2$(bpy)], (b) [Pt(SCN)(NCS)(bpy)], and (c) [Pt(NCS)$_2$(bpy)].

Table 2. Selected Bond Lengths (Å) and Angles (deg) and Nonbonded Distances (Å) of the Platinum(II) Complexes

[Pt(SCN)$_2$(bpy)]		[Pt(SCN)(NCS)(bpy)]		[Pt(NCS)$_2$(bpy)]	
Pt1−S1	2.306(4)	Pt1−S1	2.298(3)	Pt1−N1	1.994(6)
Pt1−S2	2.316(4)	Pt1−N1	2.046(6)	Pt1−N2	2.010(7)
Pt1−N1	2.05(1)	Pt1−N2	2.008(5)	Pt1−N3	1.989(7)
Pt1−N2	2.06(1)	Pt1−N4	1.979(6)	Pt1−N4	1.985(8)
S1−C11	1.69(2)	S1−C11	1.667(9)	S1−C11	1.609(9)
S2−C12	1.68(2)	S1−C12	1.618(7)	S1−C12	1.621(9)
N3−C11	1.13(2)	N3−C11	1.14(1)	N3−C11	1.15(1)
N4−C12	1.13(2)	N4−C12	1.154(9)	N4−C14	1.15(1)
S1−Pt1−S2	89.6(1)	S1−Pt1−N1	172.9(2)	N1−Pt1−N2	81.6(3)
S1−Pt1−N1	175.0(3)	S1−Pt1−N2	92.4(2)	N1−Pt1−N3	175.8(3)
S1−Pt1−N2	95.7(3)	S1−Pt1−N4	92.3(2)	N1−Pt1−N4	95.5(3)
S2−Pt1−N1	95.0(3)	N1−Pt1−N2	81.1(2)	N2−Pt1−N3	94.3(3)
S2−Pt1−N2	174.5(3)	N1−Pt1−N4	94.2(2)	N2−Pt1−N4	177.0(3)
N1−Pt1−N2	79.8(4)	N2−Pt1−N4	175.2(2)	N3−Pt1−N4	88.7(3)
Pt1−S1−C11	102.8(5)	Pt1−S1−C11	108.4(3)	Pt1−N3−C11	171.5(8)
Pt1−S2−C12	101.8(5)	Pt1−N4−C12	171.8(6)	Pt1−N4−C12	172.7(7)
S1−C11−N3	177(1)	S1−C11−N3	171.9(7)	S1−C11−N3	179.1(9)
S2−C12−N4	175(1)	S2−C12−N4	177.9(6)	S2−C12−N4	179.4(8)
Pt1···Pt1[a]	5.497(4)	Pt1···Pt1[b]	3.5939(5)	Pt1···Pt1[d]	3.237(1)
		Pt1···Pt1[c]	4.1061(5)		

[a] $x, y, z + 1$. [b] $-x, -y + 1, -z$. [c] $-x, -y, -z$. [d] $x, -y + {}^1/_2, -z$.

planar geometry including two NCS$^-$ ligands, because all the atoms lie on a crystallographic mirror plane. The difference between S- and N-coordination can also be seen in the coordination bond lengths of the bipyridine ligand. As shown in Table 2, the average distance for Pt−bpy (Pt1−N1 and Pt1−N2) is ca. 2.06 Å for [Pt(SCN)$_2$(bpy)] and 2.00 Å for [Pt(NCS)$_2$(bpy)]. Consistent with this, the coordination bond distance between Pt1 and N1, which is located *trans* to the thiocyanato-*S* ligand, is 2.05 Å, and the Pt1−N2 distance, being *trans* to the thiocyanato-*N* ligand, is 2.01 Å. These data indicate that the S-coordination affects the platinum(II) center stronger than the N-coordination and exhibits a definite *trans* effect.

Depending on their molecular structures, the isomers are accordingly stacked in the crystals. As shown in Figure 2a, the nonplanar structure of [Pt(SCN)$_2$(bpy)] yields a largely slipped stack with no Pt···Pt interactions. The Pt···Pt distances of the slightly slipped stack for [Pt(SCN)(NCS)(bpy)] also suggest minimal Pt···Pt interactions, as can be seen from Figure 2b and Table 2. On the other hand, in the case of [Pt(NCS)$_2$(bpy)], the linear chain structure with a short Pt···Pt distance, as seen in Figure 2c, clearly indicates the Pt···Pt electronic interactions as in the case of analogous (α-diimine)platinum(II) complexes.[10,18]

Table 3. Absorption and Emission Spectra for the Three Linkage Isomers

	absorption[a] solution λ_{max}/nm	emission[b]			
		rigid solution		crystal	
isomers	(ϵ/10^3 M^{-1} cm^{-1})	λ_{max}/nm	τ/μs	λ_{max}/nm	τ/μs
[Pt(SCN)$_2$(bpy)][c]	368 (7.11) 325 (24.4)	630	19	657	2.5
[Pt(SCN)(NCS)(bpy)][c]	373 (7.62) 325 (20.6)	610	23	604	2.6
[Pt(NCS)$_2$(bpy)][d]	365 (7.58) 325 (20.3)	459 494 525	6.9	708	2.0

[a] At room temperature. [b] At 77 K. [c] The solution data were measured in acetone. [d] The solution data were measured in DMF.

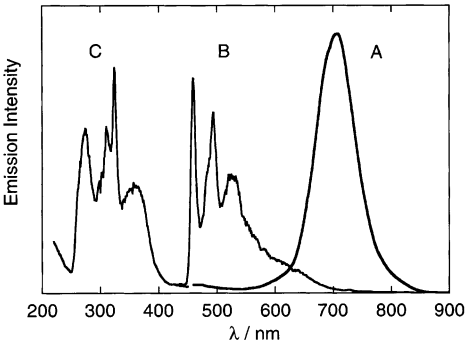

Figure 3. (A) Emission spectrum of the neat crystals of [Pt(NCS)$_2$(bpy)] (λ_{ex} = 340 nm) at 77 K and (B) emission (λ_{ex} = 340 nm) and (C) excitation (λ_{em} = 488 nm) spectra of the complex in DMF (1.4 × 10^{-5} M) at 77 K.

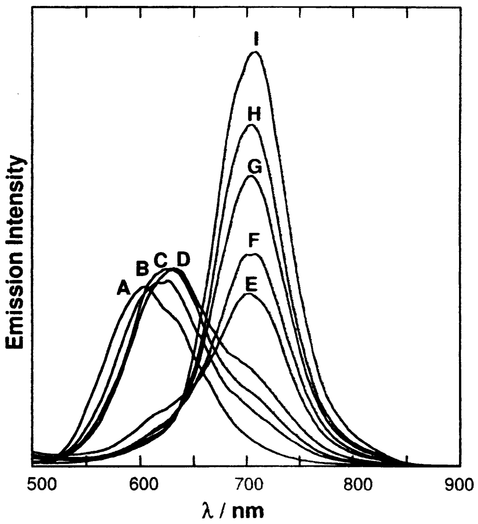

Figure 4. Emission spectral change for the neat crystals of [Pt(SCN)(NCS)(bpy)] kept at 75 °C. The emission spectra (λ_{ex} = 340 nm) were measured at 77 K after (A) 0 min, (B) 5 min, (C) 10 min, (D) 20 min, (E) 30 min, (F) 40 min, (G) 50 min, (H) 60 min, and (I) 70 min.

Emission Spectroscopy. Of the three isomers, only red crystals of [Pt(NCS)$_2$(bpy)] exhibited intense emission with a maximum at 650 nm and the lifetime of 36 ns at room temperature. At 77 K, however, all the isomers yielded characteristic luminescence. The emission maxima (λ_{max}) and the lifetimes (τ) in the rigid solution and neat crystals at 77 K, as well as the absorption data at room temperature, are summarized in Table 3.

As shown in Figure 3, the emission spectrum for [Pt(NCS)$_2$(bpy)] in a dilute solution at 77 K is quite different when compared to the emission spectrum from the solid state. The spectrum with a vibronic structure for the complex in DMF (Figure 3B) is assignable to the emission from the $^3\pi\pi^*$(bpy) state, as is typically observed for monomeric bipyridine complexes such as [Pt(bpy)$_2$]$^{2+}$ and [Pt(en)(bpy)]$^{2+}$.[19,20] The excitation spectrum (Figure 3C) is essentially consistent with the absorption spectrum. The two bands with a maximum at 274 nm and maxima at 324 and 310 nm, respectively, can be assigned to the $^1\pi\pi^*$(bpy) bands on the basis of data for many other bipyridine complexes from earlier studies.[19] The band at the longer wavelength (λ_{max} = 361 nm) can be assigned to the ^{1}MLCT transition band. As shown in Table 3, the corresponding absorption bands can be seen at similar wavelengths for all three isomers. Thus, the luminescence in the rigid solution of [Pt(NCS)$_2$(bpy)] reflects the emission state of the discrete complex.

On the other hand, the intense luminescence of the crystals appears at much longer wavelengths as shown in Figure 3A. The emission state is reasonably assigned to the ^{3}MMLCT state, taking the linear-chain structure with short Pt···Pt distances into account. The spectrum is very similar to those for the red forms of [PtCl$_2$(bpy)] and [Pt(CN)$_2$(bpy)].[18,21]

The luminescence features of [Pt(SCN)$_2$(bpy)] and [Pt(SCN)(NCS)(bpy)], however, are quite different than that for [Pt(NCS)$_2$(bpy)]. These isomers exhibit similar unstructured spectra both in the rigid solution and in the solid state. The spectra for [Pt(SCN)$_2$(bpy)] and [Pt(SCN)(NCS)(bpy)] in the solid state can be seen in Figures 4 and 5, respectively, as spectrum A. The similarity of the spectra for the rigid solution and the crystals indicates that the origin of the emission can be ascribed to the electronic state of the monomeric complex. This is also supported by the crystal structures since there are no Pt···Pt interactions for [Pt(SCN)$_2$(bpy)] and [Pt(SCN)(NCS)(bpy)]. The spectral features also resemble those reported for [Pt(SCN)(tpy)]$^+$ (tpy = 2,2′:6′,2″-terpyridine).[22] Therefore, the emission state for [Pt(SCN)$_2$(bpy)] and [Pt(SCN)(NCS)(bpy)] could be assigned to the monomeric ^{3}MLCT state or a charge-transfer state mixed with S(p) → π^*(bpy) character, as described for Pt(diimine) complexes containing S-coordinated ligands such as dithiolate.[23] It is interesting to note that the emissions for [Pt(SCN)$_2$(bpy)] and [Pt(SCN)(NCS)(bpy)] clearly have longer lifetimes when compared to the $^3\pi\pi^*$ emission for [Pt(NCS)$_2$(bpy)] as seen from Table 3.

Isomerization Behaviors in Solution and in the Solid State. During the isolation process for the three linkage

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(18) Kato, M.; Kosuge, C.; Morii, K.; Ahn, J. S.; Kitagawa, H.; Mitani, T.; Matsushita, M.; Kato, T.; Yano, S.; Kimura, M. *Inorg. Chem.* **1999**, *38*, 1638−1641.

(19) Yersin, H.; Humbs, W.; Strasser, J. *Coord. Chem. Rev.* **1997**, *159*, 325−358.

(20) Kato, M.; Takahashi, J.; Sugimoto, Y.; Kosuge, C.; Kishi, S.; Yano, S. *J. Chem. Soc., Dalton Trans.* **2001**, 747−752.

(21) Houlding, V. H.; Miskowski, V. M. *Coord. Chem. Rev.* **1991**, *111*, 145−152.

(22) McMillin, D. R.; Moore, J. J. *Coord. Chem. Rev.* **2002**, *229*, 113−121.

(23) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949−1960.

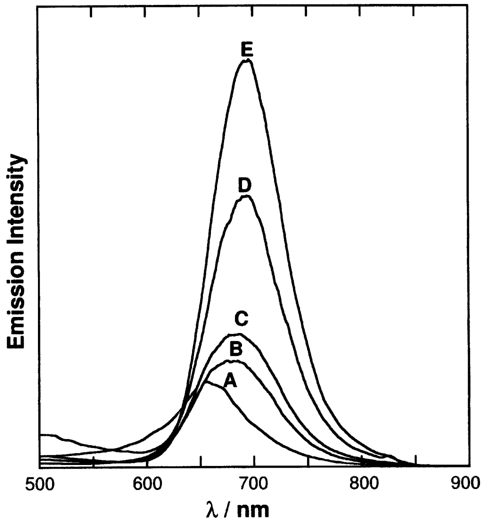

Figure 5. Emission spectral change for the neat crystals of [Pt(SCN)$_2$(bpy)] kept at 75 °C. The emission spectra (λ_{ex} = 340 nm) were measured at 77 K after (A) 0 min., (B) 10 min, (C) 20 min, (D) 30 min, and (E) 40 min.

isomers, the stability of each isomer in solution depended on the solvent. At room temperature, the isomerization occurred easily in DMSO and DMF solutions, whereas it was relatively slow in acetone and 2-butanone solutions. The isomerization behavior of the linkage isomers in DMSO-d_6 solution was studied by ^{1}H NMR spectroscopy, since the three isomers are easily distinguishable on the basis of their ^{1}H NMR data. Specifically, the chemical shift for the proton at the 6-position of the pyridine ring (H^6) varies sensitively depending on the coordination atom of the thiocyanato ligand at the *trans* position which is δ 9.37 ppm for [Pt(SCN)$_2$(bpy)], δ 9.08 and 8.80 ppm for [Pt(SCN)(NCS)(bpy)], and δ 8.73 ppm for [Pt(NCS)$_2$(bpy)]. The deshielding effect on H^6 due to the coordination becomes weaker in this order. This corresponds very well with the variation in the Pt−N bond lengths found in the crystal structures (vide supra).

Figure 6A−D shows the ^{1}H NMR spectral change of [Pt(SCN)$_2$(bpy)] on standing at 25 °C. The spectra indicate that the [Pt(SCN)$_2$(bpy)] isomer (the signals marked with *) was converted sequentially to [Pt(NCS)$_2$(bpy)] (the signals marked with •) by way of [Pt(SCN)(NCS)(bpy)] (the signals marked with #). The red precipitate of [Pt(NCS)$_2$(bpy)] was gradually deposited with increasing ratio of the [Pt(NCS)$_2$(bpy)] isomer.

The solution (at the Figure 6D stage) was then irradiated with the near UV light (330 ± 50 nm) at 25 °C. The signals for [Pt(NCS)$_2$(bpy)] decreased while those for [Pt(SCN)(NCS)(bpy)] and [Pt(SCN)$_2$(bpy)] reappeared as can be seen in Figure 6E,F. When the photoirradiation was performed using visible light (420 ± 80 nm) instead of the near UV light, the change was much slower. This indicates that the backward or reverse isomerization is lead by the photoexcitation of the monomeric complex. As in the case of many photosubstitution reactions,[24] the photoirradiation likely results in the dissociation of the ligand, and as a result, the kinetically more favorable Pt−SCN bond would be formed again.

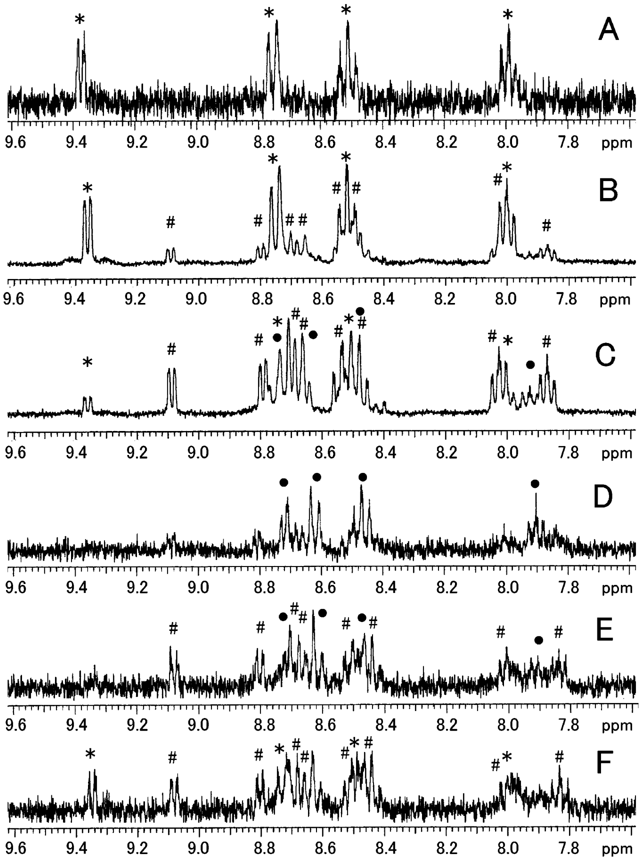

Figure 6. ^{1}H NMR spectral change of [Pt(SCN)$_2$(bpy)] in DMSO-d_6. The sample solution (ca. 5 × 10^{-4} M) was kept at 25 °C for (A) 0 min, (B) 5 min, (C) 45 min, and (D) 7 h. The sample solution was then irradiated with near UV light (330 ± 50 nm) for (E) 15 min and (F) 3 h at 25 °C. The symbols *, #, and • indicate the signals for [Pt(SCN)$_2$(bpy)], [Pt(SCN)(NCS)(bpy)], and [Pt(NCS)$_2$(bpy)], respectively.

In the solid state, a gradual change of the yellow crystals, for both [Pt(SCN)$_2$(bpy)] and [Pt(SCN)(NCS)(bpy)], to red crystals was observed. Figure 4 shows the solid-state emission spectra at 77 K when neat crystals of [Pt(SCN)(NCS)(bpy)] were kept at 75 °C. The result clearly shows that the conversion of [Pt(SCN)(NCS)(bpy)] to [Pt(NCS)$_2$(bpy)] is consistent with the color change. More interestingly, the emission spectrum of [Pt(SCN)$_2$(bpy)] changed directly to that for [Pt(NCS)$_2$(bpy)] without exhibiting the spectrum due to [Pt(SCN)(NCS)(bpy)], as shown in Figure 5. It was also confirmed by ^{1}H NMR that the red-emissive product obtained from the isomerization was [Pt(NCS)$_2$(bpy)]. Such direct isomerization from [Pt(SCN)$_2$(bpy)] to [Pt(NCS)$_2$(bpy)] is characteristic of the solid and indicates that [Pt(SCN)(NCS)(bpy)] is not generated or at least is very unstable in the isomerization process. In the solid state, there are two possibilities for structural transformation: the flip of the ligand as in the case in solution, and ligand transfer or exchange. The crystal structures of the three isomers have no close intermolecular arrangement of the thiocyanato ligands, except for one thiocyanato ligand in the crystal of [Pt(SCN)$_2$(bpy)] which is found to be oriented toward the adjacent SCN$^-$ ligand as shown in Figure 2a (S2···N4′ =

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(24) Ford, P. C. *Coord. Chem. Rev.* **1982**, *44*, 61−82.

3.85(3) Å). The arrangement, however, does not suggest the possibility of concerted ligand transfer of two SCN^- ligands in the complex. The flip of the ligands seems much easier in this arrangement. Thus, the isomerization in the solid state would occur by the flip of the ligand in the complex inducing the crystal structure transformation. The red crystals of $[Pt(NCS)_2(bpy)]$ are so stable that we could not detect any change by the photoirradiation of the crystals.

Conclusions

We have succeeded in the isolation and the structural determination of all three linkage isomers of bis(thiocyanato)-(2,2′-bipyridine)platinum(II), for the first time. Their isomerization behavior, as well as structural and luminescence properties, was elucidated in solution and in the solid state. The kinetically favorable form, $[Pt(SCN)_2(bpy)]$, was converted to the thermodynamically stable form, $[Pt(NCS)_2(bpy)]$. The flip of the thiocyanato ligands occurs stepwise in the order of $[Pt(SCN)_2(bpy)]$, [Pt(SCN)(NCS)(bpy)], and $[Pt(NCS)_2(bpy)]$ in solution, while it occurs correlatively in the solid state. In solution, the thermodynamically stable form $[Pt(NCS)_2(bpy)]$ is reconverted to [Pt(SCN)(NCS)(bpy)] and $[Pt(SCN)_2(bpy)]$ by photoirradiation. Thus, it was demonstrated that the isomerization among the three linkage isomers can be controlled thermally and photochemically.

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Supporting Information Available: Crystallographic information file (CIF) and the packing diagrams of three linkage isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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