A novel linkage isomeric pair of mixed ligand Ni(II) complexes with IM2py-κ^2N,O and IM2py-κ^2N,N modes in [Ni(acac)(tmen)-(IM2py)]$^+$; synthesis and X-ray structure

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This is the first report of a Ni(II) complex with the six-membered IM2py chelate coordinating *via* oxygen, [Ni(acac)(tmen)(IM2py-κ^2N,O)]PF$_6$ (**1·PF$_6$**) (acac = acetylacetonate; tmen = N,N,N',N'-tetramethylethylenediamine; IM2py = 2-(2-(pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy). This new complex **1·PF$_6$** has been synthesized by the direct reaction between [Ni(acac)(tmen)]PF$_6$ and IM2py. The X-ray analysis (monoclinic, $P2_1/c$, a = 15.378(2), b = 13.331(2), c = 16.560(2) Å, β = 116.377(6)°, Z = 4) demonstrated that the IM2py ligand is coordinated to Ni(II) as an unprecedent six-membered didentate chelate with the κ^2N,O mode in **1**. The corresponding linkage isomer, [Ni(acac)(tmen)(IM2py-κ^2N,N)]PF$_6$ (**2·PF$_6$**), was obtained from the deoxygenation reaction of [Ni(acac)(tmen)(NIT2py)]PF$_6$ with NaNO$_2$. Variable-temperature measurements of the magnetic susceptibility and UV-vis absorption bands indicated a ferromagnetic interaction in **2·PF$_6$** and an antiferromagentic one in **1·PF$_6$**. These facts confirm a linkage isomeric pair of [Ni(acac)(tmen)(IM2py-κ^2N,O)]$^+$ (**1**) and [Ni(acac)(tmen)(IM2py-κ^2N,N)]$^+$ (**2**) with oxygen and nitrogen coordination, respectively, in the IM moiety.

Introduction

In the course of the intensive investigations to construct molecular magnets, a number of multi-spin exchange coupled systems have been reported consisting of paramagnetic or diamagnetic metal ions and nitroxide radicals such as several derivatives of 4,4,5,5-tetramethyl-4, 5-dihydro-1H-imidazolyl-3-oxide-1-oxyl (NIT)[1,2] or 4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazol-1-oxy (IM).[3–6] Recently, we have endeavored to reveal the relation between the magnetic properties and absorption spectra of the paramagnetic metal complexes,[7–14] *e.g.*, exhibiting the coligand effect[8–11] on the magnetic interaction between the paramagnetic metal ion with various β-diketonates and the radical ligands NIT2py and/or IM2py (Scheme 1) aiming at fine-tuning the magnetic interactions. The differences in magneto-optical interactions have been thoroughly examined among the NIT2py and IM2py Ni(II) and Cr(III) complexes from the viewpoint of the overlap and orthogonality between the d_σ or d_π and the ligand π^* or π orbitals in conjunction with the metal-to-ligand SOMO π^* (MLCT) or ligand SOMO π^*-to-metal (LMCT) charge transfer transitions.[11] All the Ni(II) nitroxide radical complexes hitherto reported were coordinated by a monodentate IM-κN(IM) ligand in the IM-Me complex[3] or IM-κ^2N(IM),N(py) didentate five-membered chelate ligand in IM2py complexes.[3–6,11,12,14] This suggests that the IM2py Ni(II) complexes prefer the nitrogen coordination to the oxygen of IM or that the five-membered chelation in IM2py (Scheme 2(a)) is more favorable than six-membered chelation (Scheme 2(b)). In fact, there has been no report on IM2py-κ^2O(IM),N(py) didentate six-membered chelated complexes. If they were available, it would be of interest to reveal the difference in magneto-optical properties between the linkage isomers of the six-membered IM2py-
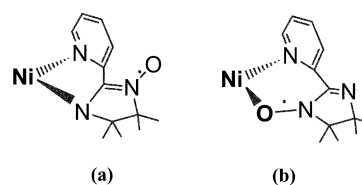
Scheme 2

κ^2N,O and five-membered IM2py-κ^2N,N complexes in both of which the MLCT may be similar to each other, having almost identical SOMO π^* orbitals.

In this paper, we report the synthesis of a linkage isomeric pair of the IM2py chelate and a comparative study on the difference in magnetic interaction with varying the magnetic orbitals between the linkage isomers.

Experimental

Synthesis

Starting complexes [Ni(acac)(tmen)(NIT2py)]PF$_6$,[8] [Ni(acac)(tmen)]PF$_6$,[15] and NIT2py,[16] IM2py[17] nitroxide radicals were synthesized according to literature methods.

IM2py-κ^2N,O complex (1). To a solution of 1 mmol of [Ni(acac)(tmen)]PF$_6$ in 50 mL of CH$_2$Cl$_2$ was added 1 mmol of IM2py with stirring at −15 °C. The formation of [Ni(acac)-(tmen)(IM2py)]$^+$ was inferred from the immediate color change of the reaction solution. After condensation of the reaction solution, the crude powder was obtained by adding *n*-heptane. Recrystallization by vapor diffusion with dichloromethane–diethyl ether gave green–red crystals, which were suitable for X-ray analysis. Anal. Calc. for C$_{23}$H$_{39}$N$_5$O$_3$NiPF$_6$: C, 43.35; H, 6.17; N, 10.99. Found: C, 43.22; H, 6.13; N, 10.92%.

IM2py-κ^2N,N complex (2). To a solution of 1 mmol of [Ni(acac)(tmen)(NIT2-py)]PF$_6$ in 50 mL of CH$_2$Cl$_2$ was added 1.02 g of NaNO$_2$ and 1 mL of CH$_3$COOH with stirring at room temperature. After 15 min stirring, the color of the solution changed from green to red. After filtration of the reaction solution, the filtrate was neutralized with NaHCO$_3$. After the

IM2py   **NIT2py**
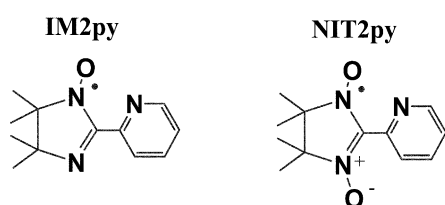
Scheme 1

reaction solution was dried by adding Na_2SO_4, it was evaporated to dryness. The residue was dissolved in 10 mL of $CHCl_3$. This solution was loaded on a HPLC (LC-908, Japan Analytical Industry Co. Ltd.) and eluted with $CHCl_3$. The first band was the desired product $[Ni(acac)(tmen)(IM2py)]^+$. After the eluate was condensed, crystallization was carried out by vapor diffusion in acetonitrile–diethyl ether. This complex was recrystallized as a red powder.

Anal. Calc. for $[Ni(acac)(tmen)(IM2py)]PF_6$ ($C_{23}H_{39}N_5O_3$-$NiPF_6$): C, 43.35; H, 6.17; N, 10.99. Found: C, 43.05; H, 6.14; N, 10.91%.

Crystallography

A green–red crystal of $[Ni(acac)(tmen)(IM2py)]PF_6$ (**1·PF₆**) with approximate dimensions of $0.45 \times 0.38 \times 0.20$ mm was glued on the top of a glass fiber with epoxy resin. The X-ray intensities ($2\theta_{max} = 55°$) were collected on an automated Rigaku AFC-5R four-circle diffractometer.

The structure was solved by the direct method using the SHELXS86 program [18a] and refined on F^2 with all independent reflections using the SHELXS97 program.[18b] All calculations were carried out using a TeXsan[19] software package.

CCDC reference number 190031.

See http://www.rsc.org/suppdata/dt/b3/b301530k/ for crystallographic data in CIF or other electronic format.

Measurements

UV-vis absorption spectra were obtained by a Perkin Elmer Lambda 19 spectrophotometer. Variable-temperature UV-vis absorption spectra were measured at 300, 280, 240 and 200 K on the same spectrophotometer with an Oxford CF1204 cryostat in CH_2Cl_2.

Magnetic susceptibility data were obtained at 2000 Oe in the range 2–300 K by using a SQUID susceptometer (MPMS-5S, Quantum Design). Pascal's constants were used to determine the constituent atom diamagnetism.

Results and discussion

Preparations and solution properties

The two complexes (**1** and **2**) were synthesized by quite different methods. When $[Ni(acac)(tmen)]PF_6$ and the IM2py radical were mixed in CH_2Cl_2 at room temperature, $[Ni(acac)(tmen)$-$(IM2py$-$\kappa^2N,O)]^+$ **1** was found to form in solution. However, during the formation reaction at room temperature, the six-membered chelate IM2py complex **1** changed gradually to the five-membered chelate IM2py complex **2**, accompanied with partial decomposition as seen from the UV-vis spectra. Therefore, low temperature conditions are required for the preparation of complex **1**. Judging from the seemingly irreversible conversion from complex **1** to complex **2** together with the stability of complex **2** in solution, complex **1** may be a metastable intermediate in which the IM2py-κ^2N,O six-membered chelate could be trapped at low temperature.

The five-membered chelated IM2py complex **2** was formed by removal of an oxygen atom in $[Ni(acac)(tmen)(NIT2py)]$-PF_6. There are two possible reaction routes: a removal of the uncoordinated oxygen or the coordinated oxygen in the NIT2py complex. So far there is no definite evidence to determine which route is operating.

The initial formation of the IM2py-κ^2N,O six-membered chelate might arise from a steric congestion of methyl groups between the coligand tmen and the IM2py-κ^2N,N chelate as inferred from molecular modelling considerations. As a result, this steric factor could block the initial N–N five-membered chelation of IM2py; leading to the initial formation of the IM2py-κ^2N,O chelation, but not of IM2py-κ^2N,N by the direct method.

Table 1 Crystallographic data for $[Ni(acac)(tmen)(IM2py)]PF_6$ (**1·PF₆**)

Formula	$C_{24}H_{39}F_6N_5NiPO_3$
Formula weight	637.27
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	15.3779(16)
b/Å	13.3309(18)
c/Å	16.5597(15)
β/°	116.377(6)
V/Å³	3041.3(6)
Z	4
D_c/g cm^{-3}	1.392
μ(Mo-Kα)/cm^{-1}	0.759
$R_1{}^a$	0.0538
$wR_2{}^b$	0.2455

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma wF_o{}^2]^{1/2}$.

Molecular structure

The crystal data is shown in Table 1 and the molecular structure of **1·PF₆** is shown in Fig. 1. This is an octahedral complex which is coordinated through the pyridyl nitrogen and imino nitroxide oxygen of the IM2py forming a six-membered κ^2N,O-chelate, in contrast to a five-membered κ^2N,N-chelation of IM2py as usually found for most IM2py complexes.[3–6,11,12]

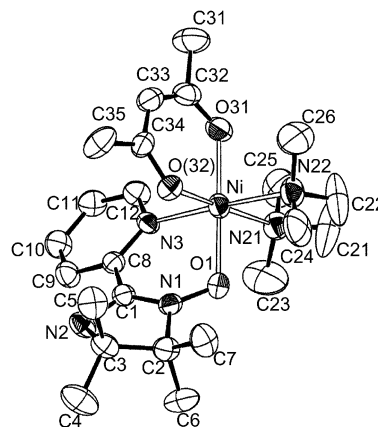**Fig. 1** View of the molecular structure of $[Ni(acac)(tmen)(IM2py$-$\kappa^2N,O)]PF_6$ (**1·PF₆**).

The dihedral angle (25.23°) between the nitroxide moiety (O(1)N(1)C(1)N(2)) relative to the pyridine plane (N(3)C(8)-C(9)C(10)C(11)C(12)) for complex **1·PF₆** is larger than that (9.63°) for $[Ni(acac)_2(IM2py$-$\kappa^2N,N)]$ (**3**)[11] and close to that (23.15°) for $[Ni(acac)(tmen)(NIT2py)]PF_6 \cdot 1/3CH_2Cl_2$ (**4·PF₆**).[8] This indicates that the IM2py chelate in **1·PF₆** is less planar than that of **3**. Around the IM2py moiety in complex **1·PF₆**, the bond angles and the dihedral angles are similar to those of **4·PF₆**. The N–O length (1.338(5) Å) of IM2py in **1·PF₆** is longer than those in complexes **3** and **4·PF₆**.

Magnetic properties

The products of the molar magnetic susceptibilities (χ_M) and temperature (T) $\chi_M \cdot T$ vs. T plot for **1·PF₆** and **2·PF₆** are shown in Fig. 2. The $\chi_M \cdot T$ products at room temperature are smaller for **1·PF₆** and larger for **2·PF₆** than the calculated values for an uncorrelated system containing a nickel(II) cation and IM2py radical ($S = 1 + 1/2$) ($\chi_M \cdot T = 1.375$ emu K mol^{-1}). The $\chi_M \cdot T$ products decrease for **1·PF₆** and increase for **2·PF₆** with lowering the temperature. This result suggests that **1·PF₆** and **2·PF₆** exhibit antiferromagnetic and ferromagnetic interaction between the Ni(II) and IM2py radical, respectively. The magnetic coupling constants J_{obs} involving nickel(II) ion and IM2py were obtained by fitting the magnetic susceptibilities χ_M to a two-spin system [20] ($H = -2JS_1 \cdot S_2$; $S_1 = 1$, $S_2 = 1/2$). The J_{obs}
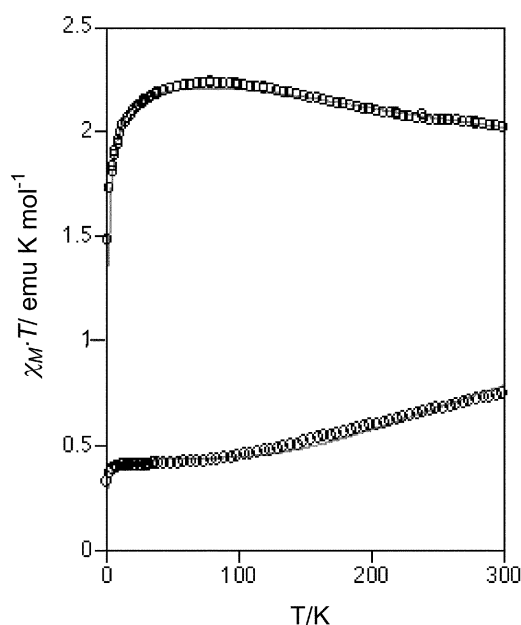
Fig. 2 Temperature dependence of the magnetic susceptibilities for [Ni(acac)(tmen)(IM2py-$\kappa^2 N,O$)]PF$_6$ (**1·PF$_6$**) (○) and [Ni(acac)(tmen)(IM2py-$\kappa^2 N,N$)]PF$_6$ (**2·PF$_6$**) (□) in the form of $\chi_M \cdot T$ *vs. T*.

Fig. 3 Absorption spectra of [Ni(acac)(tmen)(IM2py-$\kappa^2 N,O$)]$^+$ (**1**) (—), [Ni(acac)(tmen)(IM2py-$\kappa^2 N,N$)]$^+$ (**2**) (-·-) and IM2py (···) in CH$_2$Cl$_2$ at room temperature.

values of **1·PF$_6$** and **2·PF$_6$** are estimated to be -135 cm^{-1} ($g = 2.14$, $\theta = -0.570$) and 98.3 cm^{-1} ($g = 2.18$, $\theta = -0.84$) with R (= $\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma(\chi_{obs})^2$) values of 6.50×10^{-5} and 10.2×10^{-5}, respectively. The drastic change in sign of the *J* value from complex **1·PF$_6$** to **2·PF$_6$** is elucidated in relation to the dissimilarity in structure according to consideration on the basis of recent magnetic or magneto-optical studies which have been generally accepted so far;[2,3,8,10,11] *e.g.*, ferromagnetic IM2py-*k*N and antiferromagnetic NIT2py Ni(II) or Cr(III) complexes result from the orthogonality and overlap between the magnetic d(e_g) or d(t_{2g}) orbitals and radical SOMO π* orbitals, respectively.[11] That is, complexes **1·PF$_6$** and **2·PF$_6$** with planar and nonplanar chelated IM2py lead to more and less orthogonality of the magnetic orbitals between the Ni(II) and IM2py, respectively, confirming a five-membered and six-membered IM2py-$\kappa^2 N,N$ chelate which are in accordance with the situation for the NIT2py complex **4·PF$_6$**[8] and IM2py complex **3**.[10] This fact substantiates the importance of the orthogonality or overlap between the magnetic orbitals with the Ni(II) magnetic d(e_g) orbitals rather than other factors such as localization of the unpaired electron on the oxygen atom or delocalization over the ligand framework in the IM2py moiety.

The magnitude of the *J* value (98.33 cm^{-1}) for complex **2·PF$_6$** is larger than that (41.2 cm^{-1}) for complex **3**. This may arise from the displacement of acac to tmen or the coligand effect; probably exerting an increase in the ferromagnetic contribution J_F to the J_{obs} values as inferred from the examination of the mangeto-optical properties for two series of [Ni(β-diketonato)(tmen)(NIT2py)]PF$_6$ and [Ni(β-diketonato)$_2$(NIT2py)] complexes.[8] It is noted that the *J* values (-135 cm^{-1}) for complex **1·PF$_6$** is close to that ($J = -149.0$) for complex **4·PF$_6$** with the same coligands (acac and tmen), though there is no uncoordinated oxygen in the IM moiety of **1·PF$_6$** unlike in the NIT2py of **4·PF$_6$**. It is suggested that the magnetic interaction with the Ni(II) ion depends on the similarity in structure of the chelated moiety between NIT2py and IM2py, irrespective of the fact that they have each MLCT to different SOMO π* orbitals.

UV-vis spectra

Complexes **1** and **2** show differing UV-vis spectra (Fig. 3) from each other as well as from the corresponding nonradical Ni(II) complexes. For complexes **1** and **2**, the absorption bands in the
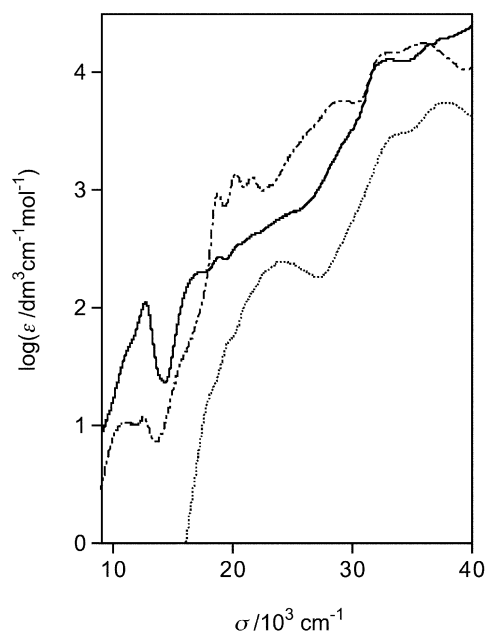
spin-forbidden $^3A_2 \longrightarrow {}^1E$ d–d transition region around 13×10^3 cm^{-1} were found to be enhanced by more than ten times as compared with those[8] of the nonradical complex [Ni(acac)(tmen)(NO$_2$)]. The intensities for **1** were much larger than those for **2**. These characteristics of the absorption spectra of **1** and **2** correspond to those observed for the NIT2py **4**[8] and IM2py **3**[10] complexes, respectively. This behavior results from the exchange couplings of the ground $^3A_2$ state and the excited ^1E state with the IM2py radical which generate the quartet ^4L_T ($^3A_2$), the doublet ^2L_T ($^3A_2$) and the doublet ^2L_S (^1E) states. Accordingly, the breakdown of the $\Delta S = 0$ restriction for the triplet–singlet spin-forbidden d–d transitions of the IM2py Ni(II) complexes gives rise to the spin-allowed transition between the exchange coupled doublets. The difference in intensity between complexes **1** and **2** is due to the Boltzmann population and depopulation of the doublet level in the ground state at room temperature, respectively. Absorption band intensity diminution and enhancement with lowering the temperature are observed (Fig. 4) for complexes **1** and **2**, respectively, as reported for the **4**[8] and **3**[10] complexes. This results from the Boltzmann depopulation and population of the doublet level in the ground state for complexes **1** and **2**,
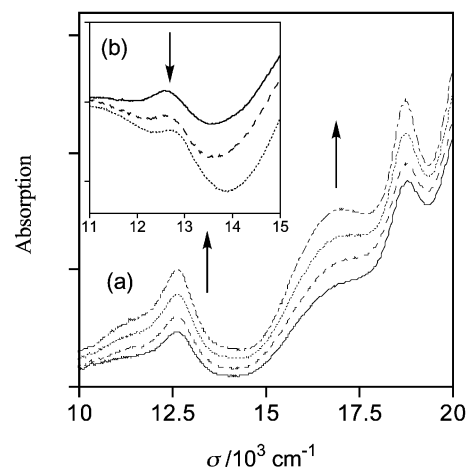

Fig. 4 Variable-temperature absorption spectra of (a) [Ni(acac)(tmen)(IM2py-$\kappa^2 N,O$)]$^+$ (**1**) and (b) [Ni(acac)(tmen)(IM2py-$\kappa^2 N,N$)]$^+$ (**2**) in CH$_2$Cl$_2$ at 300 K (-·-), 280 K (···), 240 K (---) and 200 K (—).

respectively, supporting that the lowest level in the ground state is the quartet level for **2** and the doublet level for **1**, in accordance with the ferromagnetic or antiferromagnetic interaction as observed by the magnetic susceptibility measurements.

Conclusion

A linkage isomeric pair of [Ni(acac)(tmen)(IM2py)]$^+$ with five- and six-membered chelate IM2py were successfully synthesized by different synthesis methods and characterized by X-ray analysis and/or magnetic susceptibility and variable-temperature absorption spectra. To the best of our knowledge, complex **1** is the first example of six-membered chelation with the $\kappa^2 N,O$ coordination mode being adopted by IM2py. As expected from the orbital orthogonality or overlap, the planar IM2py-$\kappa^2 N,N$ and nonplanar IM2py-$\kappa^2 N,O$ Ni(II) complexes give reversed magnetic interactions, showing ferromagnetic and antiferromagnetic interaction, respectively, with similar MLCT to mostly identical SOMO π^* in the IM2py. This evidence may provide some possibility to control the magnetic properties intentionally by tuning the coordination mode of the identical radical ligand in equilibrium situations.

Acknowledgements

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