Synthesis and Novel Spectroscopic Behavior of Octahedral Bis(β-diketonato) Complexes of Paramagnetic Cr(III) and Ni(II) Ions Containing a Nitronyl Nitroxide Radical Chelate

Takafumi Yoshida, Kan Kanamori,† Satoshi Takamizawa, Wasuke Mori,†† and Sumio Kaizaki*
Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560
†*Department of Chemistry, Faculty of Science, Toyama University, Gofuku 3190, Toyama 930*
††*Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-12*

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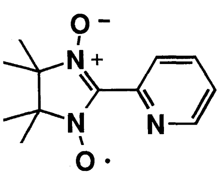
New bis(β-diketonato)Cr(III) and Ni(II) complexes with a chelating nitronyl nitroxide radical were synthesized and characterized. The intensification and/or large Stokes shift of the spin-forbidden components and the charge transfer transitions revealed by the resonance Raman spectra in the visible region were found, which result from the moderate exchange coupling.

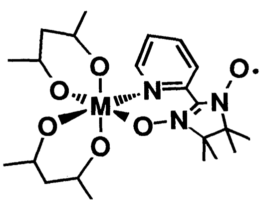
Recently, there have been a number of studies on multi-spin exchange coupled systems in transition metal complexes with dinuclear structures[1] or radical ligands[2] from respective points of view. In strongly spin-coupled semiquinone[3] and phenoxyl radical[4] Cr(III) complexes, large antiferromagnetic interactions or intensification of the spin forbidden d-d transitions have been demonstrated. In moderately coupled systems for Cr(III) or Ni(II) complexes with radicals like nitronyl nitroxides(NITR), on the other hand, the variation of coordination modes of their radicals or nonradical coligands is expected to regulate the magneto-optical behavior. However, there has been no study on spectroscopy for Cr(III) and Ni(II) radical complexes except [(3- or 4-NOpy)CrTPP][5] and [Ni(hfac)$_2$(NIT2-py)][6] which have been examined only from interests in molecular magnetism.

In this letter, we will report the synthesis and spectroscopic behavior of new bis(β-diketonato)Cr(III) and Ni(II) complexes with NIT2-py nitronyl nitroxide, 2-(2'-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazoyl-3-oxide-1-oxyl(Scheme1).

Bis(β-diketonato)(NIT2-py) Cr(III) complexes were synthesized by the following method. A mixture of 0.12 g (0.5 mmol) of NIT2-py[7] and 0.18 g (0.5 mmol) of trans-[Cr(acac)$_2$-(H$_2$O)$_2$]Cl in 40 cm^3 of acetonitrile was kept to stand with stirring at room temperature for 12 h to give a green solution. From a green eluate on SP-Sephadex C-25 column chromatography of the reaction solution with use of 0.1 mol dm^{-3} NaCl solution, a green precipitate was obtained in 40% yield by adding 0.6 g of sodium perchlorate. This was recrystallized from CH$_2$Cl$_2$ and ether, and green thin plates were obtained. The corresponding acaCl(3-chloroacetylacetonate) complex was obtained by the same method as for the acac complex.

Ni(II) complexes, [Ni(L)$_2$(NIT2-py)] (HL=Hacac,HacaCl, Hdbm(dibenzoylmethane)), were newly synthesized from the corresponding bis(β-diketonato)diaqua Ni(II) complexes in CH$_2$Cl$_2$ by the modified method of the hfac complex,[6] and recrystallized from CH$_2$Cl$_2$ and *n*-heptane. It is noted that the β-diketonato complexes other than the hfac one can be obtained against the previous claim[6] for the favorable partner of poor electrophile metal centers like the hfac complex to the nitroxides.


Scheme 1.


Scheme 2.

Each new green NIT2-py Cr(III) complex was found to be an univalent complex cation, [Cr(L)$_2$(NIT2-py)]$^+$(L=acac,acaCl), in view of the chromatographic behavior and the elemental analysis.[8] The chelation of the NIT2-py ligand(Scheme 2) is supported by isolating the anhydrous salt.

Newly prepared bis(β-diketonato) Ni(II) complexes were identified to have a chelating NIT2-py ligand like the hfac complex by the elemental analysis[8] and by the similarity of the UV-vis spectra to that of the authentic hfac complex(Figure 1).

These new Cr(III) and Ni(II) complexes are air-stable and remain unchanged in CH$_3$CN and CH$_2$Cl$_2$, respectively, at room temperature for a month. The solvolysis in aqueous-methanol(1: 1) solution of the Cr(III) complex occurs with a half-life of *ca.* 30 h to give an equilibrated mixture of cis- and trans-[Cr(acac)$_2$-(H$_2$O)$_2$]$^+$ with releasing free NIT2-py at 25 ℃.

From the temperature dependent magnetic susceptibility measurements for the NIT2-py complexes,[9] the intramolecular magnetic exchange couplings are found to be antiferromagnetic between Cr^{3+} or Ni^{2+} and NIT2-py with the estimated J values of -122 and -118 cm^{-1} for the acac and acaCl Cr(III) complexes and -238, -236, -283 cm^{-1} for the acac, acaCl, and dbm Ni(II) complexes, respectively, whereas the J value for the hfac complex was reported to be -167 cm^{-1}.[6]

The UV-vis spectra of the radical complexes show much different characteristics from those of the corresponding nonradical complexes as in Figures 1 and 2. For both the Cr(III) and Ni(II) complexes, narrow components in the d-d transition regions around 16-19x10^3 cm^{-1} appeared as inflections and peaks or shoulders. In the Raman spectra on resonance with these components in this region, the significant intensity enhancement was observed, especially for the bands at 1520 and 1468 cm^{-1}. These two bands can be assigned to the stretching vibrations of the O-N=C moiety of the NIT2-py ligand. The other enhanced peak at 614 and 610 cm^{-1} may be due to the M-O,N stretching (respectively, Cr and Ni). Thus, the observed resonance enhancement of the Raman bands implies the charge transfer character of the 16-19x10^3 cm^{-1} components, probably corresponding to the MLCT in view of the blue shift in more polar solvents.

The absorption band or shoulder at 9.8x10^3 cm^{-1} of the Ni(II) complexes is similar in intensity and position to the lowest frequency band for [Ni(L)$_2$(tmen)](tmen=*N*,*N*,*N'*,*N'*-tetramethylethylenediamine) complex. Though the lower frequency magnetic circular dichroism(MCD) band envelopes could not be measured, they are also similar in position, sign and intensity to

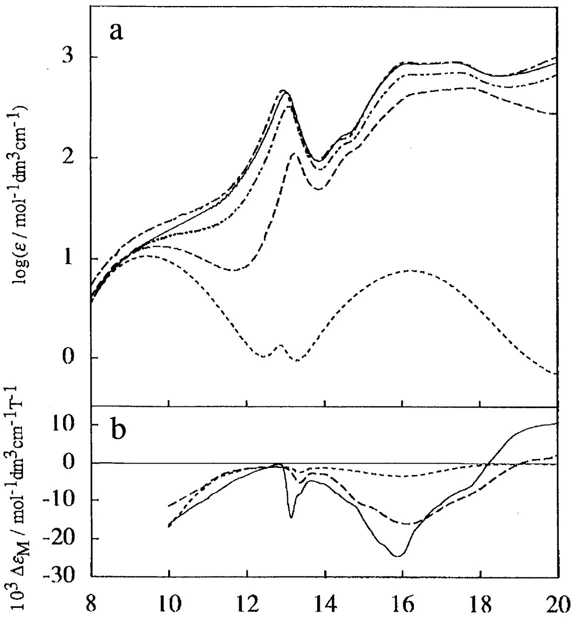


Figure 1. UV-vis(a) and MCD spectra(b) of $[Ni(L)_2(NIT2\text{-}py)]$(L=dbm(-•-•-); acac(—); acacCl(-••-••-); hfac(---) and $[Ni(acac)_2(tmen)]$(• • •) in CH_2Cl_2. MCD curves of the dbm and acacCl complexes are omitted for clarity.

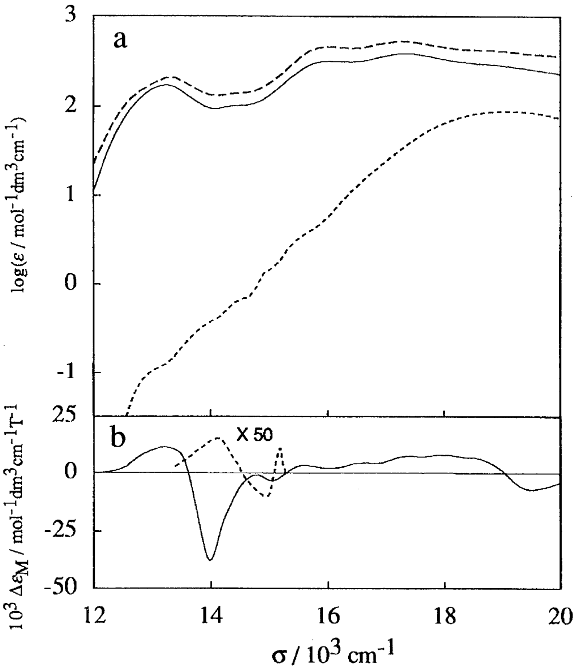


Figure 2. UV-vis(a) and MCD spectra(b) of $[Cr(L)_2(NIT2\text{-}py)]$(L=acac(—); acacCl(---) in CH_3CN and $[Cr(acac)_2(en)]$(• • •) in CH_3OH.

that of the tmen complex(Figure 1). Thus, they are assigned to the $^3T_2 \leftarrow {}^3A_2$ d-d transition, almost *unperturbed* by the radical ligand. The sharp bands at 13.0x10^3 cm^{-1} stem from the $^1E \leftarrow {}^3A_2$ spin-forbidden d-d transition, since the MCD bandwidths (*ca.* 300 cm^{-1}) are much closer to that(*ca.* 300 cm^{-1}) of the spin-forbidden transition with the same MCD sign than to that(*ca.* 2000 cm^{-1}) of the spin-allowed ones. The molar absorption coefficients(ε) are *ca.* 100 times larger than that of the tmen complex(Figure 1), and increase almost linearly with increasing the absolute J values, resulting from the exchange coupling between Ni^{2+} and the NIT2-py as theoretically anticipated.[3]

For the Cr(III) complexes, the absorption peaks near 13.4 x 10^3 cm^{-1} were intensified by a few hundreds times comapred with those of the nonradical complex $[Cr(acac)_2(en)]^+$(Figure 2). The MCD pattern in this region is similar in signs to that of $[Cr(acac)_2(en)]^+$, though their positions and intensities were different from each other as shown in Figure 2. This fact together with the expected peak positions and the similarity of the narrow MCD bandwidths(*ca.* 500 cm^{-1}) suggests that they originate from the spin forbidden $^2E, {}^2T_1 \leftarrow {}^4A_2$ d-d transitions. Such enormous intensity enhancements in the spin-forbidden transition are ascribed to the exchange coupling between the Cr^{3+} and the NIT2-py radical as demonstrated for the semiquinone[3] and phenoxyl radical[4] complexes. However, the extent of the enhancements is much smaller as inferred from the moderate magnetic couplings compared with the strong coupling case,[3,4] but is not correlated with the J values in contrast with the Ni(II) complexes.

The luminescence spectrum of $[Cr(acac)_2(NIT2\text{-}py)]ClO_4$ was observed around 12.0x10^3 cm^{-1} at the lower frequency by *ca.* 1000 cm^{-1} than the lowest frequency absorption peak. In view of this large Stokes shift as well as the ground state antiferromagnetism, the $S^* = 0$ level originating from the first ^2E excited state of Cr(III) perturbed by the radical ground state is lower than the perturbed $S^* = 1$ level; showing the antiferromagnetic coupling in the lowest excited state.

The present results provide a clue to control magneto-optical properties by modifing the radicals and/or nonradical coligands.

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References and Notes

1 P. L. McCarthy and H. U. Güdel, *Coord. Chem. Rev.*, **88**, 69(1988).
2 A. Caneschi, D. Gatteschi, and P. Rey, *Prog. Inorg. Chem.*, **39**, 331(1991).
3 C. Benelli, A. Dei, D. Gatteschi, H.U.Güdel, and L. Pardi, *Inorg. Chem.*, **28**, 3089(1989).
4 A. Sokolowski, E. Bothe, E. Bill, T. Weyhermüller, and K. Wieghardt, *J. Chem. Soc., Chem. Commun.*, **1996**, 1671.
5 M. Kitano, Y. Ishimaru, K. Inoue, N. Koga, and H. Iwamura, *Inorg. Chem.*, **33**, 6012(1994).
6 D. Luneau, G. Risoan, P. Rey, A. Grand, D. Gatteschi, and J. Laugier, *Inorg. Chem.*, **32**, 5616(1993).
7 This was prepared by the literature method: E. F. Ullman, L. Call, and J. H. Osiecki, *J. Org. Chem.*, **35**, 3623(1970).
8 Satisfactory analysis were obtained for all the complexes.
9 The magnetic susceptibilities between 4.2-300 K were analyzed by using the Hamiltonian $H=-2JS_1 \cdot S_2 (S_1, S_2 = 3/2, 1/2$ and $1, 1/2$, respectively, for Cr(III) and Ni(II) complexes).