CHEMISTRY LETTERS, pp. 1373-1376, 1987.

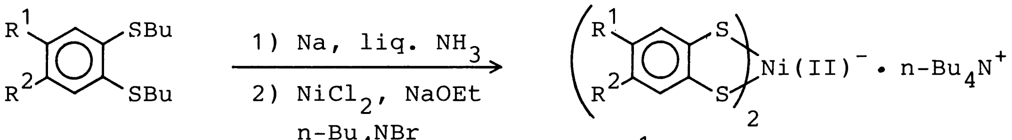
New Bis(benzene-1,2-dithiolato)Ni(II) Complexes Having Intense Near-Infrared Absorptions[1)]

Iwao TABUSHI, Kazuo YAMAMURA,* and Hiroshi NONOGUCHI
Department of Synthetic Chemistry, Kyoto University,
Sakyo-ku, Kyoto 606

New bis(benzene-1,2-dithiolato)Ni(II)•n-Bu_4N having one or two N,N-dimethylamino substituent(s) were prepared. The main characteristic in their electronic absorptions was the intense near-infrared absorption band with a maximum of intensity at 990 - 1163 nm.

Dithiolato-nickel complexes attract strong attentions because of their unique physicochemical properties and possible applications to low-dimensional conductors, $^1O_2$ quenchers or others.[2)] One of the main characteristics associated with these interesting properties of such complexes, e.g., of bis(benzene-1,2-dithiolato)-Ni(II), is the electronic absorptions with the maximum of intensity in the near-infrared (hereafter abbreviated as NIR) region,[3)] reflected by the small $2b_{1u}$(L) - $3b_{2g}$(L) transition energy(ΔE_{NIR}).[4)] For the most of these Ni complexes, however, the NIR absorption occurs at wavelength much shorter than 1 μm, suggesting the need of further studies, particularly on the relationship between structures of Ni complexes and ΔE_{NIR} or properties.

We now report a new family of bis(benzene-1,2-dithiolato)Ni(II), 1a-c, which carry NMe_2 substituent(s) at 4- (and 5-) position(s) of benzene- or toluene-1,2-dithiolato ligand (see Scheme 1). The NMe_2 substituent was found very effective to red-shift λ_{max}^{NIR} of 1a-c, among which bis(4,5-bis-N,N-dimethylaminobenzene-1,2-dithiolato)Ni(II)•n-Bu_4N (1c) was particularly interesting to exhibit the NIR absorption at 1163 nm. Its ΔE_{NIR} of 8.6×10^3 cm^{-1} is the smallest value among those of bis(benzenedithiolato)Ni complexes ever reported.

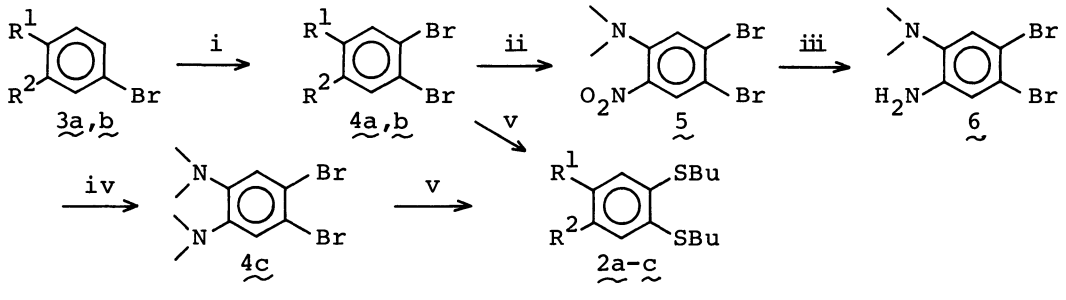


2a-c

1a-c

a) $R^1 = NMe_2$; $R^2 = H$
b) $R^1 = NMe_2$; $R^2 = Me$
c) $R^1 = R^2 = NMe_2$

Scheme 1.



i) Br_2-$AgSO_4$ ii) HNO_3-H_2SO_4 iii) Fe-HCl iv) Me_2SO_4
v) CuSBu

Scheme 2.

1,2-Bisthioethers(2a-c), the precursors to the corresponding dithio ligands, were prepared from 4-bromo-N,N-dimethylaniline(3a) or 2-methyl-4-bromo-N,N-dimethylaniline(3b) as shown in Scheme 2. Spectroscopic data for 2a-c were satisfactory (see Note 5).

3,4-Bis(n-butylsulfenyl)-N,N-dimethylaniline, 2a, was treated with 3 equiv. amount of Na in liq. NH_3.[6] After the decomposition of excess Na with NH_4Cl followed by the evaporation of NH_3, the residual dithiol was treated with (1) $NiCl_2$ (0.5 equiv.)-NaOEt(2 equiv.) then (2) n-$Bu_4\overset{+}{N}Br^-$ under Ar stream. After the air oxidation for overnight, dark green needles of bis(4-N,N-dimethylaminobenzene-1,2-dithiolato)Ni(II)·n-Bu_4N (1a) was obtained by recrystallization from $CHCl_3$-EtOH. In FAB-MS spectrum, 1a exhibited a $M+H^+$ peak at 667 m/e, and other physical data were also satisfactory, supporting the structure of 1a (see Table 1).

The most significant characteristic of Ni complex 1a was the very intense NIR absorption, λ_{max}^{NIR} of 1055 nm (ε 15400) (see also Fig. 1). Apparently, the NMe_2 substitution onto the benzene-1,2-dithiolato ligand has shifted the original NIR band ($2b_{1u}$(L) - $3b_{2g}$(L) transition[4]) to the much longer wavelength, since the corresponding parent Ni(II) complex, $(C_6H_4S_2)_2$Ni(II)·n-Bu_4N, exhibits the NIR absorption band at λ_{max}^{NIR} of 881 nm.[2a]

To investigate the red-shift of NIR absorption by NMe_2 substitution in detail, the NMe_2 group was introduced into the 5-position of bis(4-methylbenzene-1,2-dithiolato)Ni(II) or bis(4-N,N-dimethylaminobenzene-1,2-dithiolato)Ni(II) (1a)

Table 1. Properties of New Bis(benzene-1,2-dithiolato)Ni(II)·n-Bu_4N, 1a-c

	Mp θ_m/°C	IR(KBr) ν/cm^{-1}		UV - VIS in $CHCl_3$ /nm (ε)		
1a	172.5-173	430	335	264	(54400)	
				316	(42600)	
				460	(2500)	a)
1b	188-189	460	360	264	(50600)	
				318	(33100)	
				368	(10700)	a)
1c	182-184 (dec)	480	345	276	(53500)	
				318	(56600)	

a) Shoulder.

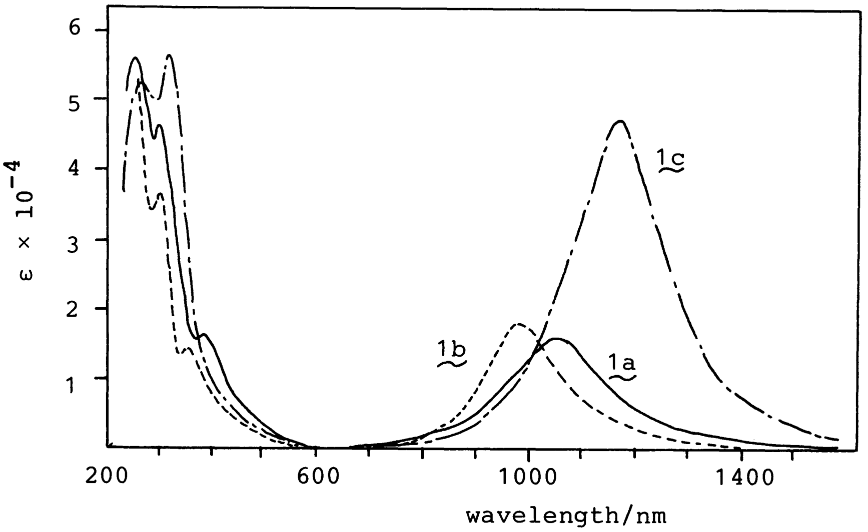


Fig. 1. The electronic absorption spectra of **1a**-**c** in the UV-VIS-NIR region.

to give **1b** or **1c**, respectively (see Scheme 1 and Table 1). The NIR transitions observed for **1b** and **1c** were λ_{max}^{NIR} = 990 nm (ε 17400) and 1163 nm (ε 46500), respectively (see also Fig. 1), strongly supporting the NMe_2 effect of decreasing the NIR transition energy. This decrease of ΔE_{NIR} probably comes from the effective conjugation between the NMe_2 moiety and the benzene-1,2-dithiolato ligand, as judged from the polarographic potential $E_{1/2}$ for the redox reaction, $[NiL_2]^{-1} \rightleftarrows [NiL_2]^0 + e^-$, of 0.07 V (**1a**), 0.20 V (**1b**), 0.0 V (**1c**) vs. Ag/AgCl in CH_2Cl_2, all of which are less positive than $E_{1/2}$ of 0.52 V for $(MeC_6H_3S_2)_2$ Ni(II) complex.[7)]

With Ni complex, **1a**, **1b**, or **1c**, was found a very effective inhibition of rubrene oxidation by $^1O_2$ which was generated by the photo-irradiation of the reported procedure.[8)] Thus, the decay rate, 2.0×10^{-7} mol dm^{-3} s^{-1}, of rubrene (initial concentration, 5.0×10^{-5} mol dm^{-3} in CH_2Cl_2) was decreased remarkably by adding 5×10^{-5} mol dm^{-3} of bis(4-N,N-dimethylaminobenzene-1,2-dithiolato)Ni (**1a**) (see Fig. 2 for the time dependent decay of rubrene). The relative decay rates of rubrene in the presence of **1a**-**c** were found as 1.0 (no quencher), 0.050 (**1c**), 0.086 (**1a**), 0.097 (**1b**), respectively. The apparent $^1O_2$ quenching rate constant, k_q, for **1c** was evaluated by the reported procedure[8)] as ca. 4×10^9 mol^{-1} dm^{-3} s^{-1}, indicating that **1c** is a very good $^1O_2$ quencher. Inhibition of dye oxidation by Ni complex, **1a**-**c**, deserves further detailed study.

A conclusion then may be drawn that the NMe_2 substituent is very effective to decrease ΔE_{NIR}, extending λ_{max}^{NIR} beyond 1000 nm for **1a** and **1c**. The small ΔE_{NIR} may give a promising property of similar Ni complexes, as exemplified by the effective inhibition of $^1O_2$ oxidation of rubrene dye reported herein.

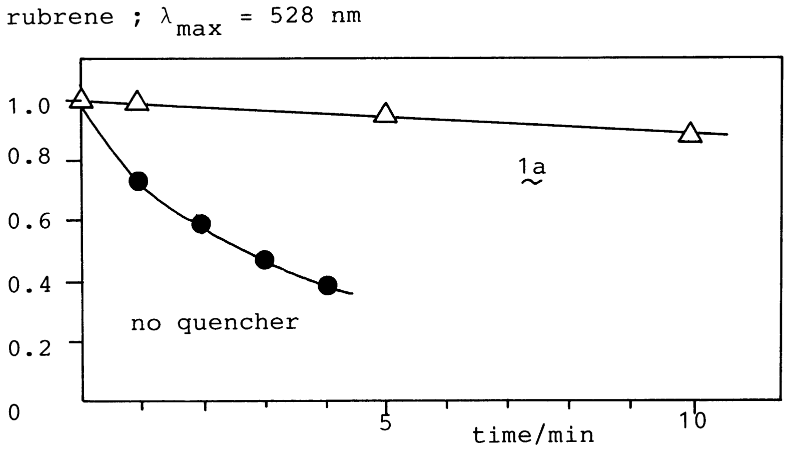


Fig. 2. Quenching of photooxidation of rubrene by bis(4-N,N-dimethylaminobenzene-1,2-dithiolato)Ni(II) (**1a**). [rubrene]= 5.0×10^{-5} mol dm^{-3} ; [**1a**] = 5.0×10^{-5} mol dm^{-3} in methylene chloride. Irradiation by a 500 W Xe lamp (>390 nm).

This work was supported in part by Japan Ministry of Education, Science, and Culture, Grant-in-Aid for Specially Promoted Research for I.T., No. 61065003.

References

1) A part of this research was presented at the 47th National Meeting of the Chemical Society of Japan, Kyoto, April (1983).
2) a) For review see e.g., J.A. McCleverty, Prog. Inorg. Chem., 10, 49 (1968); b) M.M. Ahmad and A.E. Underhill, J. Chem. Soc., Chem. Commun., 1982, 1065; c) M.M. Ahmad and A.E. Underhill, J. Chem. Soc., Dalton Trans., 1983, 165; d) M.G. Miles and J.D. Wilson, Inorg. Chem., 14, 2357 (1975); e) D.J. Carlsson, G.D. Mendenhall, T. Suprunchuk, and D.W. Wiles, J. Am., Chem. Soc., 94, 8960 (1972); f) G. Consiglio, F. Morandini, and O. Piccolo, J. Chem. Soc., Chem. Commun., 1983, 112.
3) NIR region commonly refers to the wavelength region, e.g., of 0.8 - 2.5 μm.
4) D.C. Olson, V.P. Meyweg, and G.N. Schrauzer, J. Am. Chem. Soc., 88, 4876 (1966). See also M.J. Baker-Hawkins, E. Billig, and H.B. Gray, J. Am. Chem. Soc., 88, 4870 (1966).
5) **2a** : MS m/e (rel. int.) 299 (M+2, 2), 298 (M+1, 5), 297 (M, 32) ; ^{1}H NMR ($CDCl_3$) δ 7.3, 6.7, 6.5, 3.0, 2.9, 1.9-1.2, 1. -0.7.
2b : MS m/e (rel. int.) 313 (M+2, 11), 312 (M+1, 22), 311 (M, 100); ^{1}H NMR ($CDCl_3$) δ 7.2, 7.0, 3.1-2.6, 2.7, 2.3, 1.9-1.2, 1.0-0.8.
2c : MS m/e (rel. int.) 342 (M+2, 11), 341 (M+1, 22), 340 (M, 100); ^{1}H NMR ($CDCl_3$) δ 7.0, 3.3-2.7, 2.8, 1.9-1.2, 1.1-0.7.
6) Cf. A. Ferretti, Org. Synth., Col. Vol. V, 419 (1973).
7) F.Roehrsheid, A.L. Balch, and R.H. Holm, Inorg. Chem., 5, 1542 (1966).
8) a) Ref. 2e; b) B.M. Monroe and J.J. Mrowca, J. Phys. Chem., 83, 591 (1979).

(Received April 23, 1987)