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Efficient Synthesis and Structure of Bis[acetonitrile(11,13-dimethyl-1,4,7,10-tetraaza-10,13-cyclotridecadien-12-ylidene)nickel(II)] Perchlorate

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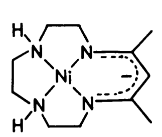
Synopsis. The titled binuclear nickel(II) complex has been synthesized by the oxidation of 11,13-dimethyl-1,4,7,10-tetraaza-10,13-cyclotridecadienatonickel(II) perchlorate with iron(III) perchlorate in deoxygenated CH_3CN in *ca.* 70% yield and its structure has been determined.

Cunninghum *et al.* reported a synthesis of $[NiI(Me_2[13]dienN_4ylidene)]_2I_2$ (**2b**), a dimer of $[Ni(Me_2[13]dienatoN_4)]^+$ (**1**),[1] though the yield was as low as less than a few percent.[2] In the formation of such a dimer, the combination of radicals formed at the γ-position of the six-membered diiminato chelate ring, *i.e.*, one electron oxidation of the coordinated ligand and the further oxidation of the bridging C–C bond to a C=C double bond should take place.[3] The low yield of the preparation of **2b** by Cunninghum's method is caused by the occurrence of side reactions such as ligand dehydrogenation and ligand oxygenation. Such reactions have been known to take place in the oxidation of **1** with Br_2[4] and in the oxidation of $[Co(Me_2[14]dieneN_4)]^{2+}$.[5]



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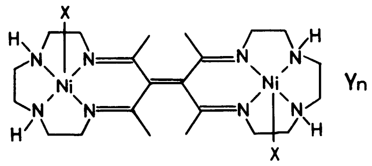

2a: X=CH_3CN Y=ClO_4^- $n=4$
2b: X=Y=I^- $n=2$
2c: X=Y=NCS^- $n=2$

In the present study, the titled nickel(II) complex has been efficiently synthesized by the oxidation of $[Ni(Me_2[13]dienatoN_4)](ClO_4)$ (**1**) in deoxygenated CH_3CN with ion(III) perchlorate, selected as an appropriate and noncoordinating oxydizing agent.[6] In this reaction, the side reactions were suppressed substantially. The dimeric structure of the oxidation product has been confirmed by X-ray analysis as well as a measurement of FD-mass spectra.

To confirm the formation of a radical at the γ-position by the oxidation with ion(III) ions, cyclic voltammograms of $[M(Me_2[X]dienatoN_4)](ClO_4)$ (M=Ni, Cu; X=13, 14) in CH_3CN were measured. Irrespective of kinds of the metal ions, these complexes showed similar irreversible waves with strong anodic peaks (E_{pa}) but did not give corresponding cathodic peaks ($i_{pc}=0$). Heights and positions of the anodic peaks were scan rate dependent. The electrochemical data were:[7] E_{pa}(M=Ni, X=13)=+0.64 V, E_{pa}(M=Ni, X=14)=+0.64 V, E_{pa}(M=Cu, X=13)=+0.50 V, E_{pa}(M=Cu, X=14)=+0.56 V. These E_{pa} values are in the narrow range of +0.5—+0.7 V and are definitely more negative than $E_{1/2}$ values of Ni^{II}/Ni^{III} couples reported for other macrocyclic nickel(II) complexes (see below).[3,8] A number of tetraaza macrocyclic nickel(II) complexes, which do not have a delocalized six-membered chelate ring, have been known to show quasi-reversible waves ($i_{pc}/i_{pa}\simeq1$) in cyclic voltammograms at $E_{1/2}$=+0.7—+1.3 V in CH_3CN. The waves correspond to Ni^{II}/Ni^{III} couples.[3,8] Furthermore, the constant electrolysis of $[Ni(Me_4[14]tetraenatoN_4)]^{2+}$, which has the delocalized six-membered rings, at +0.65 V in CH_3CN give the dimeric complex.[9] These facts suggest strongly that the observed waves are attributed to radical formations at the γ-positions. On the basis and from the observed E_{pa} values, we chose $Fe(ClO_4)_3\cdot6H_2O$ ($E_{1/2}$(II)/(III)=+1.1 V *vs.* SCE in CH_3CN[10]) as the oxidizing agent in the preparation of the titled complex.

Figure 1 shows the structure of **2a** and Table 1 lists bond lengths and angles of interest. The complex has an inversion center at midpoint of the C(12)–(12′) bond. The bridge head carbons, C(12) and C(12′), are connected by a double bond to produce a binuclear complex. In the present complex an acetonitrile molecule is coordinated to each nickel(II) ion in five-coordinate fashion. Perchlorates are not involved in coordination. In view of bond lengths and angles, C(12)–C(12′), N(1)–C(13), and N(10)–C(11) are double bonds. Four methyl groups produce large strain to C(12)–C(12′) double bond,[2] so that the double bonds are almost completely localized and the entire complex adopts a chair-like structure as in dodecachloroheptafluvalene.[11] The skeletal structure in **2a** is very similar to that reported for the iodo complex **2b**.[2]

The absorption spectrum of $[Ni(CH_3CN)(Me_2[13]$-

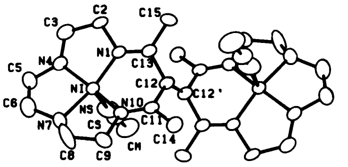

Fig. 1. Structure of $[Ni(CH_3CN)(Me_2[13]dienN_4ylidene)]_2^{4+}$ (**2a**).

TABLE 1. SELECTED BOND LENGTHS (l/Å) AND ANGLES (ϕ/°)

Ni-N(1)	1.857(6)	C(12)-C(12′)	1.366(12)
Ni-N(4)	1.898(7)	C(13)-N(1)	1.271(9)
Ni-N(7)	1.913(7)	C(11)-N(10)	1.262(9)
Ni-N(10)	1.865(6)	Ni-N(s)	2.510(8)
C(11)-C(12)-C(12′)		119.5(7)	
C(11)-C(12)-C(13)		116.0(7)	
C(13)-C(12)-C(12′)		118.9(7)	

TABLE 2. FRACTIONAL COORDINATES($\times 10^4$)[a)]

Atom	x	y	z
Ni	2139(1)	1565(1)	−275(1)
Cl(1)	1359(2)	1269(2)	−3318(2)
Cl(2)	921(2)	4494(2)	2486(2)
N(1)	863(4)	2078(5)	−632(4)
N(4)	2483(6)	3162(6)	−125(8)
N(7)	3524(5)	1214(6)	−176(6)
N(10)	1931(4)	13(5)	−649(4)
C(2)	816(6)	3347(6)	−841(6)
C(3)	1841(9)	3823(9)	−671(12)
C(5)	3550(7)	3326(9)	100(9)
C(6)	4091(8)	2275(9)	−224(10)
C(8)	3686(7)	251(11)	−807(11)
C(9)	2861(6)	−603(8)	−871(7)
C(11)	1100(6)	−483(6)	−775(5)
C(12)	207(6)	168(7)	−432(6)
C(13)	104(6)	1430(6)	−771(5)
C(14)	920(6)	−1685(7)	−1257(7)
C(15)	−877(6)	1825(8)	−1260(7)
O(1)	1521(8)	1326(7)	−4332(5)
O(2)	2131(6)	1700(9)	−2701(6)
O(3)	680(9)	2110(15)	−3171(8)
O(4)	1109(15)	270(9)	−3026(7)
O(5)	702(7)	5619(7)	2852(7)
O(6)	1437(12)	3985(10)	3286(12)
O(7)	1398(18)	4570(15)	1675(13)
O(8)	133(8)	3928(11)	2246(14)
N(S)	1892(7)	1409(9)	1574(6)
C(M)	1492(10)	1170(11)	3431(7)
C(S)	1741(8)	1322(8)	2359(6)

a) Estimated standard deviations are in parentheses.

dienN$_4$ylidene)]$_2$ClO$_4$)$_4$ in Nujol mull shows a broad band around 500 nm, characteristic of five-coordinate species.

Data of absorption spectra and molar conductivities of **2b** suggest the presence of five-coordinate species in acetonitrile and aqueous solutions.[12)]

By using the present synthetic procedures, a relatively large amount of **2a** can be obtained. Iodo and thiocyanato derivatives, **2b** and **2c** were prepared successfully from **2a** and characterized (see Experimental).

Experimental

Materials. [Ni(Me$_2$[13]dienatoN$_4$)](ClO$_4$) (**1**) was synthesized according to the literature.[13)]

[Ni(CH$_3$CN)(Me$_2$[13]dienN$_4$ylidene)]$_2$(ClO$_4$)$_4$ (**2a**): Through an acetonitrile solution (50 cm^3) containing 2.0 g of **1** was bubbled a stream of N_2 gas for 30 min to remove dissolved oxygen. To the solution was added gradually 2.5 g of Fe(ClO$_4$)$_3\cdot$6H$_2$O dissolved in a small amount of acetonitrile. N_2 bubbling was continued for further 30 min. After standing the solution in an open beaker overnight, red brown prismatic crystals formed were filtered and washed with minimum amount of acetonitrile (yield, *ca.* 70%). Found: C, 30.63; H, 4.74; N, 13.63%. Calcd for $Ni_2C_{26}H_{46}N_{10}O_{16}Cl_4$: C, 30.80; H, 4.57; N, 13.99%. IR (Nujol mull, cm^{-1}) 1651 (C=N); MS(FD), *m/e*, 833 ([Ni(Me$_2$[13]dienN$_4$ylidene)]$_2$(ClO$_4$)$_3$$^+$). The complex easily releases acetonitriles and absorbs water in the air to produce [Ni(Me$_2$[13]dienN$_4$ylidene)]$_2$(ClO$_4$)$_4\cdot$2H$_2$O. This complex was also prepared in the same manner as described above by use of water (pH=*ca.* 2 with HClO$_4$) in place of acetonitrile. Found: C, 27.32; H, 4.20; N, 11.59%. Calcd for $Ni_2C_{22}H_{44}N_8O_{18}Cl_4$: C, 27.30; H, 4.58; N, 11.58%. UV$_{max}$(CH$_3$CN) 362 nm (ε 3510) 420 nm (shoulder); Molar conductivity (Ω^{-1} cm^2 mol^{-1}) Λ(H$_2$O, 2.50$\times$10^{-4} mol dm^{-3}, pH 4.7, 25 °C) 476.

[NiX(Me$_2$[13]dienN$_4$ylidene)]$_2$X$_2$ (X=I$^-$(**2b**), NCS$^-$(**2c**)) were prepared by use of anion exchange resin (Amberlite IRA-410) at pH<3. **2b**: Found: C, 25.19; H, 3.97; N, 10.58%. Calcd for $Ni_2C_{22}H_{40}N_8I_4$: C, 25.37; H, 3.87; N, 10.76%. IR (Nujol mull, cm^{-1}) 1632 (C=N); UV$_{max}$(CH$_3$CN) 550 nm (broad); Λ (H$_2$O, 2.50$\times$10^{-4} mol dm^{-3}, pH 5.4, 25 °C) 368. **2c**: Found: C, 40.26; H, 5.24; N, 21.58%. Calcd for $Ni_2C_{26}H_{40}N_{12}S_4$: C, 40.75; H, 5.26; N, 21.93%. IR (Nujol mull, cm^{-1}) 1651 (C=N), 2075 (N=C=S); Λ (H$_2$O, 2.41$\times$10^{-4} mol dm^{-3}, pH 5.4, 25 °C) 353.

Other materials used were reagent grade.

X-Ray Analysis. The procedures used for data collection (a Rigaku AFC-5 diffractometer, Mo $K\alpha$) as well as the method used in the solution and refinement of the structure were standard and have been described previously.[14)] Crystal data: Monoclinic, P2$_1$/n, a=13.533(2), b=11.471(1), c=93.76(1)°, V=2060.2(6) Å^3, z=2, D_x=1.64 g cm^{-3}, R=0.087 for 2857 independent reflections with $F_o>3\sigma(F_o)$ ($2\theta<60°$). Table 2 lists atomic coordinates.[15)] Hydrogen atoms are not included in the calculation.

Measurements. Absorption spectra were measured with a Hitachi 340 spectrophotometer. A conductometer E518 (Metrohm Herisau) was used. Cyclic voltammograms were recorded with a Yanagimoto Polarographic Analyzer P-1100. Half wave potentials at 25 °C measured with three-electrode system were refered to SCE.

References

1) Ligand abbreviations: Me$_2$[13]dienatoN$_4$=11,13-dimethyl-1,4,7,10-tetraaza-10,13-cyclotridecadienato; Me$_2$[14]dienatoN$_4$=5,7-dimethyl-1,4,8,11-tetraaza-4,7-cyclotetradecadienato; Me$_2$[14]dieneN$_4$=5,7-dimethyl-1,4,8,11-tetraaza-4,7-cyclotetradecadiene; [Me$_2$[13]dienN$_4$ylidene]$_2$=12,12′-bi(11,13-dimethyl-1,4,7,10-tetraaza-10,13-cyclotridecadienylidene); Me$_4$[14]tetraenatoN$_4$=6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraaza-5,8,14,17-cyclotetradecatetraenato.

2) J. A. Cunningham and R. E. Sievers, *J. Chem. Soc.*, **95**, 7183 (1973).

3) J. F. Endicott and B. Durham, "Coordination Chemistry of Macrocyclic Compounds," ed by G. A. Melson, Plenum Press, New York (1979), Chap. 6.

4) C. J. Hipp, L. F. Lindoy, and D. H. Busch, *Inorg. Chem.*, **11**, 1988 (1972).

5) J. A. Switzer and J. F. Endicott, *J. Am. Chem. Soc.*, **102**, 1181 (1980); J. A. Switzer, J. F. Endicott, M. A. Kalifa, F. P. Rotzinger, and K. Kumar, *ibid.*, **105**, 56 (1983).

6) Analogous products were obtained by the oxidation of [Ni(Me$_2$[14]dienatoN$_4$)](ClO$_4$) with iron(III) ions in a similar way.

7) The E_{pa} values are given in *vs.* SCE, Et$_4$NClO$_4$=0.1 mol dm^{-3}, scan rate=500 mV s^{-1}, glassy carbon electrode.

8) K. Barefield, F. V. Lovecchio, N. E. Tokel, E. Ochiai, and D. H. Busch, *Inorg. Chem.*, **11**, 283 (1972); D. C. Olson and J. Vasilevskies, *ibid.*, **8**, 1611 (1969); F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).

9) F. C. McElroy and J. C. Dabrowiak, *J. Am. Chem. Soc.*, **98**, 7112 (1976).

10) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852, (1957).

11) M. Ishimori, R. West, B. K. Teo, and L. F. Dahl, *J. Am. Cehm. Soc.*, **93**, 7101 (1971).

12) [Ni(Me$_2$[13]dienN$_4$ylidene)]$_2$$^{4+}$ (**2a**) shows a complicated pH-dependence in aqueous solution.

13) S. C. Cummings and R. E. Sievers, *Inorg. Chem.*, **9**, 1131 (1970).

14) H. Ito, J. Fujita, K. Toriumi, and T. Ito, *Bull. Chem. Soc. Jpn.*, **54**, 2988 (1981).

15) The F_o-F_c data and thermal parameters kept are in the office of the Chemical Society of Japan (Document No. 8410).