CHEMISTRY LETTERS, pp. 697-700, 1988.

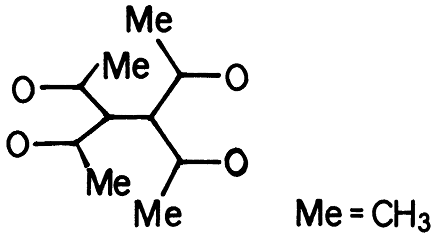
Syntheses of Nickel(II) Dinuclear Complexes with Tetraketone and the Effect of Anions on Coordination Geometries

Yutaka FUKUDA* and Kumiko MAFUNE

Department of Chemistry, Faculty of Science, Ochanomizu University,
Otsuka, Bunkyo-ku, Tokyo 112

Three nickel(II) mixed ligand dinuclear complexes were prepared, $Ni_2(tae)(tmen)_2X_2 \cdot nH_2O$ where tae = tetraketonate; tmen = N-alkylethylenediamine; $X^- = B(C_6H_5)_4^-$, ClO_4^-, or NO_3^-; n = 0 or 3. Each complex assumes the unique combination of square planar and octahedral coordination geometries in the dinuclear entity.

A 1,1,2,2-tetraacetylethanate dianion[1)] (tae, see Structure 1) is a potentially tetradentate ligand to form a dinuclear complex with metal ions.[2)] Although there were many reports about the complexes with linear polyketonate ligands such as triketonate and tetraketonate,[3)] there were not so many works with this branched tetraketonate ligand.[2)] In this study, we have synthesized three nickel(II) mixed complexes with the tetraketonate (tae) and N,N,N',N'-tetramethylethylenediamine(tmen) showing the following formula: $Ni_2(tae)(tmen)_2X_2 \cdot nH_2O$, where $X^- = B(C_6H_5)_4^-$, ClO_4^- or NO_3^-, and n=0 or 3.


tae
Structure 1

The perchlorate, $Ni_2(tae)(tmen)_2(ClO_4)_2 \cdot 3H_2O$ and the nitrate, $Ni_2(tae)(tmen)_2(NO_3)_2$, were prepared by mixing ethanolic solutions of the appropriate nickel(II) salt, tae and tmen with 2:1:2 molar ratio. The tetraphenylborate, $Ni_2(tae)(tmen)_2(B(C_6H_5)_4)_2$, was prepared from the nitrate by adding sodium tetraphenylborate(solid) to the 1,2-dichloroethane(DCE) solution of the nitrate with vigorous stirring. All the complexes were recrystallized from DCE.

Elemental analyses of the complexes are shown in Table 1 with some other properties. The tetraphenylborate and the nitrate are anhydrous. The perchlorate contains three water molecules from the analytical data. This has been confirmed by TG-DTA analysis using a thermal analytical equipment Shinku-Riko TGD-3000 (heating rate: 1 °C/min, in static air). The data of this thermal weight loss during the temperature range 60-85 °C showed that the perchlorate contained $2.9H_2O$.

The red color of the tetraphenylborate suggests the square planar coordination of both nickel(II) ions. In fact, this complex is diamagnetic (see in Table 1) and its solid reflectance spectrum shown in Fig. 1 has a main single peak at 20.8×10^3 cm^{-1} due to a square planar d^8 Ni(II) transition.[4] On the other hand, in the case of the perchlorate the magnetic moment per molecule

Table 1. Colors, analytical and magnetic data of the complexes obtained

Complex[a]	Color	C(%)[b]	H(%)[b]	N(%)[b]	Magnetic moment[c] (μ_{eff}/B.M.)	
1	Red	70.82 (70.98)	7.70 (7.15)	4.91 (4.73)	Diamagnetic	
2	Reddish-brown	33.38 (33.07)	6.24 (6.31)	6.69 (7.01)	3.14	2.44[d]
3	Bluish-green	39.33 (39.44)	6.79 (6.62)	12.58 (12.54)	4.56	3.22[d]

a) 1 ; $Ni_2(tae)(tmen)_2(B(C_6H_5)_4)_2$, 2 ; $Ni_2(tae)(tmen)_2(ClO_4)_2 \cdot 3H_2O$, 3 ; $Ni_2(tae)(tmen)_2(NO_3)_2$. b) Calculated values are shown in the parentheses. c) At room temperature. d) Magnetic moments per nickel.

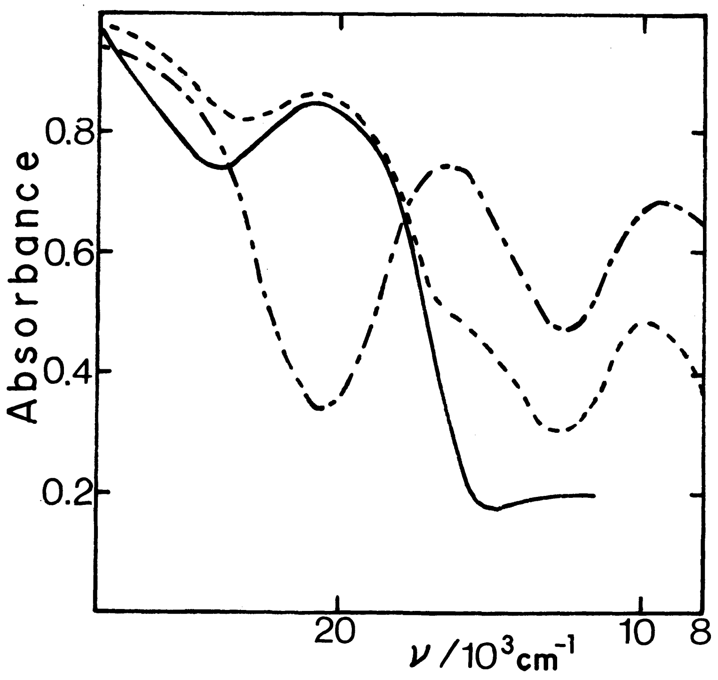
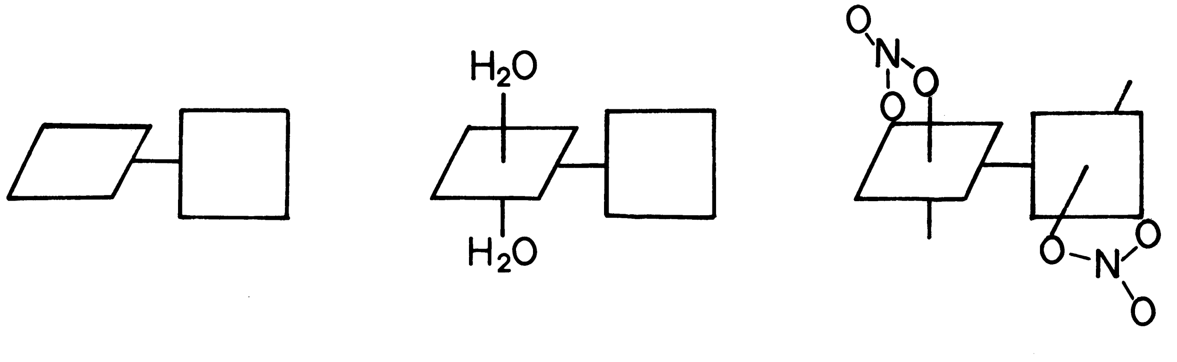


Fig. 1. Solid reflectance spectra of the complexes, 1 (——);tetraphenylborate, 2 (----); perchlorate, 3 (-·-·); nitrate.

falls in the range of atomic magnetic moment of Ni(II) octahedral species (see in Table 1). This means that one Ni(II) moiety is a square planar structure (diamagnetic) and another one is an octahedral structure(paramagnetic) in the dinuclear complex. The IR data of the perchlorate with a JASCO IR-A3 spectrophotometer by Nujol mull method show no splitting of the strong and broad band at 1100 cm^{-1} and of the strong and sharp band at 620 cm^{-1}, indicating that the ClO_4^- anion acts only as a counter ion. Solid reflectance spectrum of the perchlorate shows the existence of two nickel species due to the planar and the octahedral coordinations. The absorption maximum for planar Ni(II) moiety exists at 20.8×10^3 cm^{-1} which resembles closely that of the tetraphenylborate shown above, and the other two peaks at ca. 16×10^3 (shoulder) and 9.8×10^3 cm^{-1} are attributable to the octahedral species containing two coordinated water molecules. The latter spectral bands are similar to those of the nitrate (vide infra). The nitrate is green crystals. The magnetic moment suggests the octahedral coordination for both nickel(II) ions. Solid reflectance spectrum of this complex shows a typical octahedral pattern with peaks at 9.5×10^3 cm^{-1} and at 16.4×10^3 cm^{-1} and there is no absorption peak at ca. 20×10^3 cm^{-1} due to the square planar nickel(II) moiety(see in Fig. 1). The band due to NO_3^- in the region 1700-1800 cm^{-1} splits into two components (1770 and 1720 cm^{-1}). These bands have been used for the diagnosis of the coordination mode of the NO_3^- anion.[5)] According to Lever et al., (1) ionic nitrate shows no splitting on this band. (2) The splitting of this band being less than ca. 25 cm^{-1} shows the unidentate nitrate coordination mode, and (3) the splitting more than ca. 20 cm^{-1} indicates the bidentate coordination. From the criterion, in this case, it is clear that each nitrate ion in the dinuclear complex acts as a bidentate ligand which is the same as in the case of the mononuclear mixed chelate [Ni(acac)(tmen)(NO_3)] reported before,[6)] where acac represents acetylacetonate bidentate ligand.



1 2 3

Fig. 2. Possible structures of three dinuclear complexes, 1 ; tetraphenylborate, 2 ; perchlorate, 3 ; nitrate.

In conclusion, each of the present three complexes with a general formula, $Ni_2(tae)(tmen)_2X_2 \cdot nH_2O$, has a different combination of square planar and octahedral coordination geometries in the dinuclear entity. (1) Both nickel(II) moieties have a square planar structure and diamagnetic. The tetraphenylborate ions act only as the counter ion, $[(tmen)Ni(tae)Ni(tmen)](B(C_6H_5)_4)_2$. (2) The square planar-octahedral complex in which two kinds of nickel(II) geometries are present, i.e., the square planar form and the octahedral one containing two coordinated water molecules. The perchlorate ions also act only as the counter ion, $[(tmen)Ni(tae)Ni(tmen)(H_2O)_2](ClO_4)_2 \cdot H_2O$. (3) The octahedral-octahedral dinuclear complex in which both of the nickel(II) are octahedral containing the bidentate nitrate ligand, $[(NO_3)(tmen)Ni(tae)Ni(NO_3)(tmen)]$.

The authors wish to thank Professor Kozo Sone of Ochanomizu University for his valuable discussion and continuous encouradgements throughout this work.

References

1) R.G.Charles, Org. Synth., Coll. Vol. 4, 869 (1963).
2) D.F.Martin, W.C.Fernelius, and M.Shamma, J. Am. Chem. Soc., **81**, 130 (1959); Y.Nakano and Y.Yoshikawa, ibid., **106**, 429 (1984); M.Bassetti and L.M.Vallarino, Inorg. Chim. Acta, **105**, 135 (1985).
3) R.W.Kluiber and J.W.Lewis, J. Am. Chem. Soc., **82**, 5777 (1960); D.E.Fenton, R.R.Schroeder, and R.L.Lintvedt, ibid., **100**, 1931 (1978); D.E.Fenton and R.L.Lintvedt, ibid., **100**, 6367 (1978); R.L.Lintvedt and N.Ahumad, Inorg. Chem., **21**, 2356 (1982).
4) Y.Fukuda and K.Sone, J. Inorg. Nucl. Chem., **34**, 2315 (1972); K.Sone and Y.Fukuda, "Inorganic Thermochromism (Inorganic Chemistry Concept Vol. 10)," Springer, Heidelberg (1987).
5) A.B.P.Lever, E.Montovani, and B.S.Rȧmaswamy, Can. J. Chem., **49**, 1957(1971); Y.Ihara, Y.Fukuda, and K.Sone, Bull. Chem. Soc. Jpn., **59**, 1825 (1986).
6) Y.Fukuda, R.Morishita, and K.Sone, Bull. Chem. Soc. Jpn., **49**, 1017 (1976).

(Received January 20, 1988)