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New Observation of 5-Coordinate Dinuclear Complexes with 1,1,2,2-Tetraacetylethanate and N-Alkylated Diethylenetriamine

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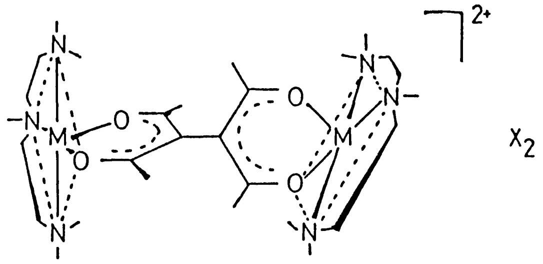
Seven dinuclear mixed ligand complexes of Ni(II) and Cu(II) containing tetraketonate(taet) and pentamethyldiethylenetriamine(Me_5dien) were synthesized, M_2(taet)(Me_5dien)$_2X_2 \cdot nH_2O$. The structures of these dinuclear complexes change between 5-coordinate (C_{4v}-C_{4v}) and 6-coordinate (Oh-Oh) ones depending upon the anion coordinating power and the metal ions used.

The branched tetraketonate ligand can form dinuclear mixed ligand complexes with various kinds of partner ligands. Recently, we prepared nickel(II) dinuclear complexes containing this type of tetraketonate such as 1,1,2,2-tetraacetylethanediide(taet) and N,N,N',N'-tetramethylethylenediamine(tmen); general formula Ni_2(tmen)$_2$(taet)$X_2 \cdot nH_2O$.[1)] These dinuclear complexes show structural varieties among 4-coordinate(square planar)-4-coordinate(square planar) (abbreviated as Sp-Sp), 6-coordinate(octahedral)-6-coordinate(octahedral) (Oh-Oh) and 4-coordinate-6-coordinate (Sp-Oh) structures. To get more different structural varieties of dinuclear mixed ligand complexes, we have tried to use N,N,N',N'',N''-pentamethyldiethylenetriamine(Me_5dien, 2,5,8-trimethyl-2,5,8-triazanonane) as a counter ligand instead of N-alkylated ethylenediamine, and to obtain 5-coordinate-5-coordinate dinuclear complexes with the general formula, M_2(Me_5dien)$_2$(taet)X_2 (Structure 1), where M=Cu(II) or Ni(II), X=ClO_4^-, NO_3^-, Cl^- or NCS^-, in this study.



Structure 1

The ligand of H_2taet was synthesized according to the literature,[2)] and the procedure to synthesize the dinuclear complexes with taet and

Table 1. Analytical Data, Colors and Magnetic Moments of M_2(taet)-(Me_5dien)$_2X_2\cdot nH_2O$. Calculated values are in parentheses

M=Ni	n	C %	H %	N %	Color	μ_{eff}/M (B.M.)
X=ClO_4	0	38.59(39.15)	6.58(6.80)	9.60(9.78)	Light Green	3.24
X=NO_3	1	42.13(41.92)	7.12(7.54)	13.82(13.97)	Green	3.12
X=Cl	1.5	44.67(44.36)	8.06(8.11)	10.96(11.09)	Yellow Green	3.15
X=NCS	1	45.68(45.36)	7.32(7.61)	14.90(14.10)	Greenish Blue	3.16
M=Cu						
X=ClO_4	0	38.02(38.71)	6.55(6.73)	9.77(9.67)	Light Green	1.77
X=NO_3	1.5	40.42(40.97)	7.34(7.49)	13.66(13.65)	Dark Green	1.73
X=Cl	2	43.10(43.29)	7.41(8.04)	10.83(10.82)	Green	1.69

Me_5dien is very similar to that applied in the previous papers,$^{1,3)}$ i.e., corresponding simple salt such as $NiX_2\cdot nH_2O$ or $CuX_2\cdot nH_2O$, tetraketone with twice molar amounts of KOH, and Me_5dien were mixed together in ethanol(EtOH) with 2:1:2 molar ratio. Then the white precipitates (KX) appeared were filtered off and the solution was concentrated. The crude crystals obtained were recrystallized from 1,2-dichloroethane (DCE). But, unfortunately, we could not obtain the Cu(II) dinuclear complex with NCS^- anion as crystals in this study.

Elemental analysis, colors and magnetic data of the complexes obtained are shown in Table 1, among which both of the Ni(II) and Cu(II) perchlorate complexes are anhydrous and other complexes contain water of crystallization. The content of these water molecules was confirmed by TG-DTA thermal analysis. These complexes did not show any color change during the thermal dehydration, which means that the water molecules in these complexes do not coordinate to the central metal ions.

The anion coordination modes are inferred from the IR data of these complexes. The perchlorate and nitrate ions do not coordinate to the central metal ions, i.e., very broad and strong band at 1100 cm^{-1} and sharp and strong band at 620 cm^{-1} indicate the ionic ClO_4^-, and the nitrate complexes have a weak single band at 1740 cm^{-1} which also shows the presence of the ionic nitrate.$^{4)}$ IR spectra of the complex, Ni_2(taet)(Me_5dien)$_2$(NCS)$_2$, show a single sharp band at 2100 cm^{-1}, which means this anion coordinates to the metal ion as a monodentate ligand through the N-donor atom.$^{5)}$ Magnetic data of copper(II) complexes show that there is no strong metal-metal interaction in the system and data of Ni(II) analogues indicate also the normal values expected for the 5- or 6-coordinate geometries.$^{6)}$

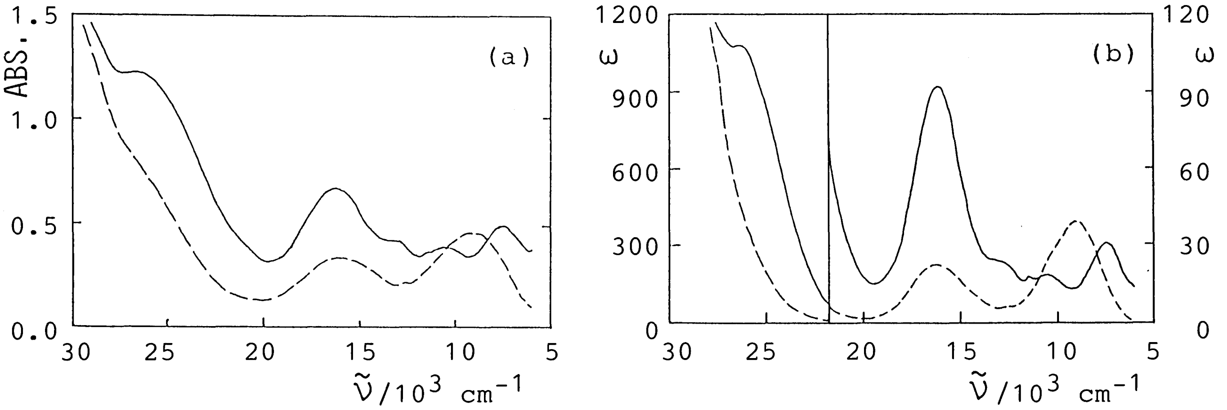
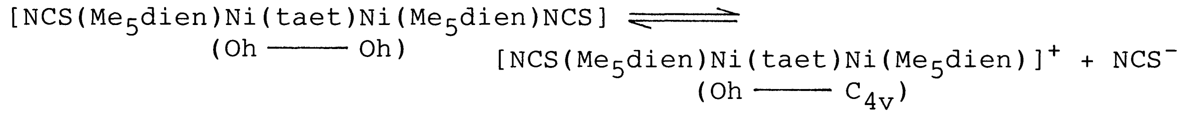


Fig. 1. (a) Solid reflectance spectra and (b) Absorption spectra in DCE of $Ni_2(taet)(Me_5dien)_2X_2$; solid line for $X=ClO_4$ and dotted line for X=NCS.

Figure 1 shows solid reflectance spectra of the dinuclear Ni(II) complexes with ClO_4 and NCS anions and the absorption spectra of these complexes in an inert solvent(DCE). The spectra of the perchlorate show the typical spectral pattern of 5-coordinate-5-coordinate (C_{4v}-C_{4v}) species without further coordination of an anion (ClO_4^-) and solvent molecules. They are very similar to the spectral pattern of the mononuclear Ni(II) complex with acetylacetonate(acac) and Me_5dien, [Ni(acac)(Me_5dien)]ClO_4, which has the square pyramidal structure (C_{4v}) confirmed by X-ray crystal analysis.$^{6)}$

In the case of the NCS-complex, however, it is easily understandable from the spectral data of the dinuclear complex in the solid state and in the inert solvent (DCE) that the coordination geometry of the complex is Oh-Oh with the coordination of the NCS^- anions.$^{7,8)}$ This is also supported by the electric conductivity measurement of the complex in DCE, from which this NCS-complex is a non-electrolyte ($\Lambda_M=0.48$ S cm^2 mol^{-1}). On the other hand, in the strong acceptor solvent with weak donor properties like nitromethane, this Ni(II)-NCS complex exists as an equilibrium mixture between 5- and 6-coordination with liberation of the anion NCS^-. The absorption peak in the nitromethane solution at 16.2 x 10^3 cm^{-1} increases much more than that in the DCE solution, which is due to the partial formation of 5-coordinate species. From the electric conductivity data, the NCS^- ligand dissociates up to about 30% in the nitromethane solution.$^{9)}$ The existence of the dissociated anion NCS^-



$$\underset{(Oh \text{——} Oh)}{[NCS(Me_5dien)Ni(taet)Ni(Me_5dien)NCS]} \rightleftharpoons \underset{(Oh \text{——} C_{4v})}{[NCS(Me_5dien)Ni(taet)Ni(Me_5dien)]^+} + NCS^-$$

was also supported from the data of FT-IR measurements. The $\nu_{C\equiv N}$ band of the NCS-complex in DCE showed at 2095 cm^{-1} due to the coordinated NCS^-. In the nitromethane solution two peaks at 2098 cm^{-1} with strong intensity and 2061 cm^{-1} with weak intensity were observed; the former and the latter bands are due to the coordinated and the ionic NCS^-, respectively, because of the high acceptor properties of the solvent used. This is an interesting example of dinuclear mixed ligand complexes with the 5-coordinate-5-coordinate structure and also the rare structural change from Oh-Oh coordination to C_{4v}-C_{4v} due to the change of anion coordination power.

For the spectral comparison of the Cu(II) dinuclear systems, there is no big change in the coordination geometry among these complexes with different anions such as perchlorate, nitrate and chloride ions. These results reflect that the Cu(II) ion can form 5-coordinate complexes more easily than the Ni(II) ion.[10)]

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References

1) Y. Fukuda and K. Mafune, Chem. Lett., **1988**, 697.
2) R. G. Charles, Org. Synth., Coll. Vol. 4, 869 (1963).
3) J. Labuda, K. Mafune, and Y. Fukuda, Bull. Chem. Soc. Jpn., **63**, 2610 (1990).
4) Y. Fukuda, C. Fujita, H. Miyamae, H. Nakagawa and K. Sone, Bull. Chem. Soc. Jpn., **62**, 745 (1989).
5) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed, John-Wiley & Sons, New York (1978).
6) N. Shintani, Y. Fukuda, Y. Ohashi, and K. Sone, Bull. Chem. Soc. Jpn., in press (1991).
7) For 6-coordinate spectra of Ni(II), see A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam (1968).
8) K. Sone and Y. Fukuda, "Inorganic Thermochromism," Springer, Heiderberg (1987).
9) W. J. Geary, Coord. Chem. Rev., **7**, 81 (1971).
10) K. F. Purcell and J. C. Kotz, "An Introduction to Inorganic Chemistry," Holt-Saunders, Tokyo (1980), Chaps. 9, 10.

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