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Characterization and Classification of 'Tervalent Nickel Complexes', $Ni(diamine)_2ClX_2$ ($X = Cl$ and ClO_4)

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The ESR, magnetic susceptibilities, IR and electronic spectra, and electric conductivities of solid state were measured for a series of nickel complexes of the general formula $Ni(diamine)_2ClX_2$ *which appeared to contain 'tervalent nickel' in order to elucidate the oxidation state of the nickel. Based on these data they were characterized and classified into the following three groups. A)* $Ni(en)_2Cl_3$ *and* $Ni(tn)_2Cl_3$*, low-spin* d^7 *Ni(III) complexes; B)* $Ni(pn)_2Cl_3$*,* $Ni(cyn)_2Cl_3$*,* $Ni(btn)_2Cl_3$ *and* $Ni(en)_2Cl(ClO_4)_2$*, Ni(II)–Ni(IV) mixed valence complexes; and C)* $Ni(phn)_2Cl_3$*, probably Ni(II) complex with cation radical ligand.*

Introduction

Although relatively few 'tervalent nickel complexes' have been reported, their electronic states and structures have attracted much attention among coordination chemists in recent years. 'Tevalent nickel complexes' so far reported are those with ligands such as phosphines [1], arsines [2], dithiolates [3], oximes [4], diamines [5], N_4-macrocycles [6], fluorides [7], peptides [8], and so on. However, the authenticity of the Ni(III) state does not seem to be established for all those compounds. Even if the compounds appear to be Ni(III) complexes based on the empirical formula, they could belong to the following groups:

A) intrinsic nickel(III) complexes
(*e.g.*, $[Ni(cyclam)Cl_2]ClO_4$) [9]
B) Ni(II)–Ni(IV) (1:1) mixed valence complexes
C) Ni(II) complexes with cation radical ligand
($[Ni(diars)_2Cl_2]Cl$) [2]
D) partially oxidized complexes
($Ni(dpg)_2I$) [10]

In 1965 Babaeva *et al.* [5] reported the syntheses of $Ni(en)_2Cl_3$, $Ni(pn)_2Cl_3$ and $Ni(en)_2Cl(ClO_4)_2$, where $Ni(en)_2Cl_3$ is paramagnetic but $Ni(pn)_2Cl_3$ and $Ni(en)_2Cl(ClO_4)_2$ are diamagnetic. Though mononuclear Ni(III) complexes cannot be diamagnetic, Babaeva *et al.* did not further investigate the cause of the diamagnetism of the complexes.

In the present study, on the basis of ESR, magnetic susceptibilities, IR and electronic spectra, and electric conductivities of solid state, we have characterized the structures and electronic states of the 'tervalent nickel complexes', such as $Ni(A–A)_2ClX_2$ (A–A = 1,2-diaminoethane (en), 1,3-diaminopropane (tn), 1,2-diaminopropane (pn), 1,2-diaminocyclohexane (cyn), 2,3-diaminobutane (btn), and *o*-diaminobenzene (phn), X = Cl and ClO_4), where $Ni(tn)_2Cl_3$, $Ni(cyn)_2Cl_3$, $Ni(btn)_2Cl_3$ and $Ni(phn)_2Cl_3$ were newly prepared.

As a result, the compounds were classified into the three groups (A, B and C in the above classification). The characterization of Ni(II)–Ni(IV) mixed valence complexes is the first case.

Experimental

Syntheses

$Ni(en)_2Cl_2$ was prepared after *Inorg. Synth.* [11] Other complexes of the $Ni(A–A)_2Cl_2$ type were prepared by similar procedures to that for $Ni(en)_2Cl_2$ [12].

The preparative methods of $Ni(A–A)_2Cl_3$ were similar to that described by Babaeva *et al.* A typical example is shown below.

$Ni(cyn)_2Cl_3$

When Cl_2 was bubbled in an absolute methanol solution (50 ml) of $Ni(cyn)_2Cl_2$ (1 g) for several minutes, luster dark blue microcrystals immediately precipitated, which were filtered, washed with absolute methanol and dried in a vacuum desiccator over P_2O_5.

For the preparation of $Ni(en)_2Cl(ClO_4)_2$ the procedure was the same as that of Babaeva *et al.* in principle but we used 70% $HClO_4$ instead of 60%

TABLE I. Elemental Analyses of Complexes.

	Found % (Calcd. %)			
	Ni	C	H	N
$Ni(en)_2Cl_3$	21.00(20.58)	16.59(16.84)	5.63(5.65)	19.26(19.64)
$Ni(tn)_2Cl_3$	19.21(18.74)	23.51(23.00)	6.58(6.43)	17.56(17.88)
$Ni(pn)_2Cl_3$	19.14(18.74)	23.02(23.00)	6.56(6.43)	17.53(17.88)
$Ni(cyn)_2Cl_3$	14.27(14.19)	36.31(36.63)	7.25(7.17)	13.89(14.27)
$Ni(btn)_2Cl_3$	17.11(17.20)	27.90(28.15)	6.98(7.09)	16.01(16.41)
$Ni(en)_2Cl(ClO_4)_2$	14.63(14.21)	11.51(11.63)	3.89(3.90)	13.32(13.56)

TABLE II. Classification of 'Tervalent Nickel Complexes'.

	μ_{eff} (B.M.)		$g_\parallel$	$g_\perp$	ν_{max} ($\times 10^3$ cm^{-1})	Color
	298 K	77 K				
$Ni(en)_2Cl_3$	1.89	1.81	2.020	2.20	23.8	greenish brown
$Ni(tn)_2Cl_3$	1.99	1.95	2.034	2.19	24.4	greenish brown
$Ni(pn)_2Cl_3$	0.56	0.46	–	–	15.2	luster dark blue
$Ni(cyn)_2Cl_3$	0.52	0.43	–	–	15.2	luster dark blue
$Ni(btn)_2Cl_3$	0.50	0.47	–	–	15.4	luster dark blue
$Ni(en)_2Cl(ClO_4)_2$	0.90	0.78	–	–	16.9	greenish black
$Ni(phn)_2Cl_3$	–	–	2.004		–	red

$HClO_4$. The employment of 70% $HClO_4$ has much improved the yield and purity of the product.

All the above compounds could not be recrystallized, because they are insoluble in all organic solvents available and decompose in water.

Elemental analyses of carbon, hydrogen and nitrogen were carried at the Elemental Analyses Service Center, Kyushu University. Metal analyses were done with a Shimadzu atomic absorption flame spectrometer Model 610S (Table I).

Measurements

Infrared spectra were measured with a Hitachi 215 infrared spectrometer on a nujol mull. Absorption spectra were measured with a Shimadzu multipurpose spectrometer Model MSP-5000 on a nujol mull.

Magnetic susceptibilities were measured by the Faraday method at ambient and liquid nitrogen temperatures. The apparatus was calibrated with $HgCo(NCS)_4$ [13]. Effective magnetic moments were calculated by using the formula, $\mu_{eff} = 2.828 \sqrt{\chi_A \cdot T}$ where χ_A is magnetic susceptibility per atom corrected for diamagnetism for all the constituent atoms by the use of Pascal's constants [14].

ESR spectra were measured with a JES-ME-3X spectrometer using an X-band on powder samples at liquid nitrogen temperature.

Electric conductivity was measured for a pellet by the four-prove dc method. Four wires were attached to the pellet with silver conducting paste as electrodes. When an applied voltage of 10 V and a standard resistance of 10^9 Ω were used, resistance up to 10^{12} Ω could be measured. The samples were maintained in a pumped vacuum during all measurements.

Results and Discussion

Effective magnetic moments, g-values obtained from ESR, the lowest-energy bands of electronic spectra (ν_{max}), and colors of the 'tervalent nickel complexes' are listed in Table II. These complexes were characterized and classified into the following three groups based on these data.

A-group; $Ni(en)_2Cl_3$ and $Ni(tn)_2Cl_3$.

These compounds show magnetic moments which are in conformity with those of one unpaired electron. Powder ESR spectra, shown in Fig. 1, are similar

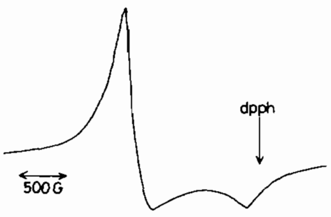

Fig. 1. ESR spectrum of $Ni(en)_2Cl_3$ in powder at liquid nitrogen temperature.

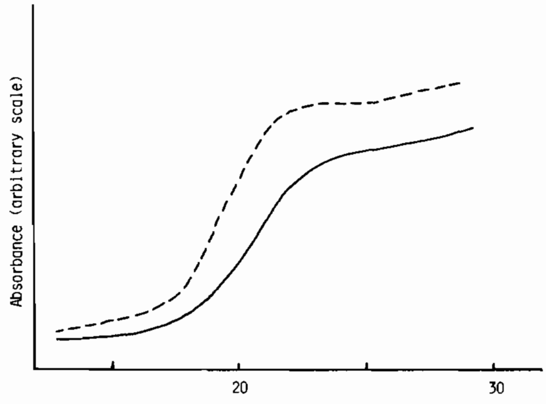

Fig. 2. Electronic spectra (in nujol mull) of $Ni(en)_2Cl_3$ (– – –) and $Ni(tn)_2Cl_3$ (———).

in spectral pattern ($g_\perp > g_\parallel \approx 2$) to those of low-spin Co(II) complexes with one unpaired electron in d_{z^2} orbital [15]. The electronic spectra (Fig. 2) are quite different from those of the group B compounds (Fig. 4), but are similar to those of dihalogenomacrocyclic tetraamine Ni(III) complexes [6].

It is known that *trans*-dichlorobis(ethylenediamine) complexes has one strong band of $\delta(NH_2)$ at about 1600 cm^{-1}, while $\delta(NH_2)$ of the *cis* isomer splits into two [16]. The IR spectra of these complexes show only one strong band near 1600 cm^{-1}, indicating that they are *trans* isomers. Therefore, these complexes are low-spin d^7 *trans*-$[Ni(A{-}A)_2Cl_2]Cl$.

B-group; $Ni(pn)_2Cl_3$, $Ni(cyn)_2Cl_3$, $Ni(btn)_2Cl_3$ *and* $Ni(en)_2Cl(ClO_4)_2$.

The complexes belonging to this group show low magnetic moments at room and liquid nitrogen temperatures as seen in Table II. There was observed a trend for all the B-group complexes that μ_{eff} at liquid nitrogen temperature is a little lower than that at room temperature. This trend cannot be attributed to the antiferromagnetic interaction between paramagnetic nickel(III) ions, because such interaction would bring about a much more sudden decrease in μ_{eff} in going from 300 K to 77 K. The observed paramagnetism may be best interpreted as being due to a slight amount of paramagnetic impurity mainly consisting of Ni(II) or Ni(III) ions. Therefore the complexes of this group are most probably mixed valence species similar to the Pt(II)–Pt(IV) mixed valence complexes of the general formula $[Pt(A{-}A)_2][PtCl_2(A{-}A)_2]Y_4$ ($Y = ClO_4$ and BF_4), which were proved by X-ray diffraction analyses [17–21]. In fact, all B-group complexes show a strong absorption in the visible region (at about 16 × 10^3 cm^{-1}) (Fig. 4), which should be an intervalence charge-transfer band, as was expected from the analogy of the spectra of teh Pt(II)–Pt(IV) mixed valence complexes.

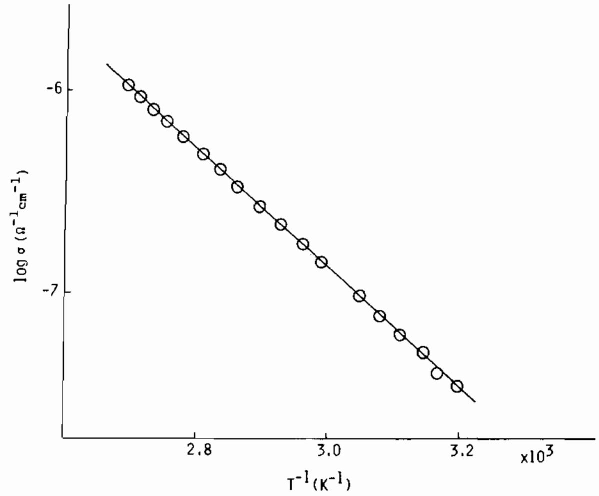

Fig. 3. Temperature dependence of conductivity of $Ni(en)_2Cl(ClO_4)_2$ (pellet).

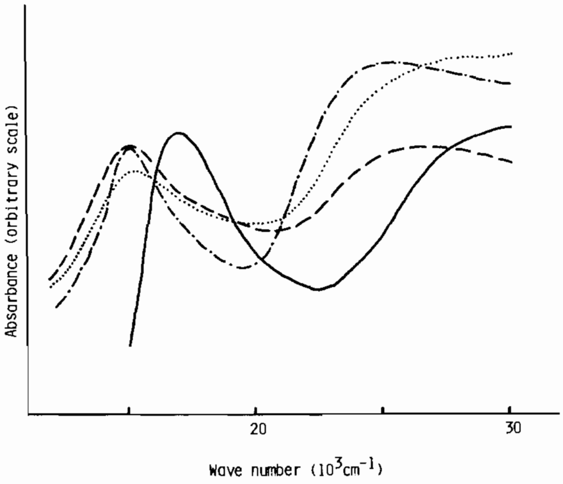

Fig. 4. Electronic spectra (in nujoll mull) of $Ni(en)_2Cl(ClO_4)_2$ (———), $Ni(pn)_2Cl_3$ (– – –), $Ni(btn)_2Cl_3$ (–·–·–) and $Ni(cyn)_2Cl_3$ (·······).

Electric conductivities of B-group complexes were measured on a pellet over a temperature range from 25 °C to 80 °C (Table III). Figure 3 shows the

TABLE III. Results of Conductivity Measurements on Pellets.

	25 °C (Ω^{-1} cm^{-1})	activation energy (eV)
$Pt(en)_2I(ClO_4)_2$ [23]	3.0×10^{-9}	0.51
	$(1.8 \times 10^{-8})^a$	$(0.42)^a$
$Pd(en)_2Br(ClO_4)_2$ [23]	1.2×10^{-8}	0.50
$Ni(en)_2Cl(ClO_4)_2$	1.3×10^{-8}	0.58
$Ni(cyn)_2Cl_3$	2.6×10^{-7}	0.24
$Ni(pn)_2Cl_3$	1.3×10^{-7}	0.35

[a] Measured on single crystal.

results of the conductivity measurement of $Ni(en)_2Cl(ClO_4)_2$ as a function of temperature from 25 °C to 80 °C. A plot of log σ *vs.* 1/T shows a linear relationship. The activation energy of conductivity was determined from the slope of the curve as defined by the equation $\sigma = \sigma_0 \exp(-\Delta E/kT)$ [22], where σ = conductivity and ΔE = activation energy. From the above results we may conclude that the complexes of this group have structures similar to those of the platinum and palladium mixed valence complexes which are known as linear chain semi-conductors as was shown in the preceeding paper [23].

C-group; $Ni(phn)_2Cl_3$

The powder ESR spectrum at 77 K shows only one signal about g = 2 with the half height width of 20 G, suggesting the presence of a radical species. Hence, this compound is likely to be a nickel(II) complex with *o*-diaminobenzene cation radical. The width (20 G) is larger than those of organic radical species. This is probably due to the perturbation from the unpaired electrons of nickel(II) ion.

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