

Synthesis and Characterization of Copper(II) and Nickel(II) Complexes of 1,5-Diamino-3-pentanol and Its Derivatives

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Dihydrochloride of a binucleating ligand, 1,5-diamino-3-pentanol (Hdpl·2HCl) has been synthesized by a new method in a high yield (>70%). This ligand forms 1 : 1 complexes with copper(II), Cu(dpl)X (X = BF₄, ClO₄, NO₃, and Cl(H₂O)). The cryomagnetic study of the copper complexes has shown that they are binuclear, and a strong antiferromagnetic interaction is operating between two copper ions. The binuclear structure seems to be quite stable even in aqueous solution. The 1 : 1 complex with nickel(II) was also isolated as tetraphenylborate, which was essentially diamagnetic. A planar binuclear structure similar to the copper complexes was assumed for this complex. Its absorption band at $29.8 \times 10^3 \text{ cm}^{-1}$ ($\epsilon = 160$) was attributed to the charge transfer transition from the bridging oxygen to the nickel similarly to the bands in the $25\text{--}29 \times 10^3 \text{ cm}^{-1}$ region usually observed for alkoxo-oxygen bridged binuclear copper(II) complexes. Some 2 : 1 copper(II)–dpl complexes have also been synthesized and characterized as binuclear complexes. 1,5-Bis(dimethylamino)-3-pentanol has been synthesized, and its 2 : 1 copper(II) complexes have been isolated.

It is well known that linear aliphatic amino alcohols such as $\text{R}_2\text{N}(\text{CH}_2)_n\text{OH}$ and $\text{R}_2\text{N}(\text{CH}_2)_m\text{NH}(\text{CH}_2)_n\text{OH}$ (R = alkyl; m and $n = 2$ or 3) form bi-, tri-, and tetra-nuclear complexes with copper(II).^{1–7)} The complexes have been extensively studied for their magnetisms, spectra,^{3–7)} and structures.^{8–16)} Since they are limited to those bridged with terminal alkoxo-oxygen atoms, they are readily hydrolyzed in water forming mononuclear species. In connection with the increasing attention to binuclear copper complexes in view of the elucidation of the function of copper protein, it has been desired to prepare binuclear copper complexes which are soluble and stable in water. The purpose of this study is to prepare such complexes with a saturated aliphatic amino alcohol. One of the reasons to adopt the saturated amino alcohol as a ligand is that it is transparent throughout the region of conventional electronic spectral measurements; this would facilitate the spectroscopic study of the complex with this ligand.

The molecular model investigation has revealed that the most suitable ligand for our purpose is 1,5-diamino-3-pentanol (abbreviated as Hdpl), which is capable of forming 6-6-membered fused chelate rings involving two metal ions bridged by an alkoxo-oxygen atom (*cf.*, Fig. 1-a). In this study we have succeeded in preparing the 1 : 1 binuclear copper(II) complexes with dpl which are stable even in aqueous solution. This ligand also enabled us to prepare the 1 : 1 binuclear nickel(II) complex similar to the copper complexes.

Alkoxo-oxygen bridged binuclear copper(II) complexes generally show an absorption band in the $23\text{--}28 \times 10^3 \text{ cm}^{-1}$ region which is attributed to a charge transfer transition from bridging oxygen to copper.²⁾ Such a band is naturally expected for the binuclear copper(II) complexes with dpl. It is interesting to see if a similar band is observed for the nickel complex, since planar binuclear nickel(II) complexes bridged by alkoxy-oxygen atoms have not been reported so far.

The ligand Hdpl was already prepared as a picrate by Taniyama *et al.*,¹⁷⁾ but the yield was so poor that it

was difficult to prepare enough sample for the synthesis of metal complexes. Hence, in this study we have exploited a new synthetic route to this ligand with a high yield (>70%). This enabled us to prepare the new complexes as reported in this paper.

Experimental

Syntheses. *1,5-Diamino-3-pentanone Dihydrochloride:* To a suspension of potassium phthalimide (370 g, 2 mol) in 1.3 dm³ of dry *N,N*-dimethylformamide (DMF), crude 1,5-dichloro-3-pentanone¹⁸⁾ (240 g, 1.3 mol) was added dropwise in 1 h with vigorous stirring. The temperature spontaneously rose from 15 °C to 65 °C during the addition, and the mixture was further heated at 80–85 °C for 6 h and allowed to stand overnight at room temperature. The resulting 1,5-diphthalimido-3-pentanone was collected by filtration and washed successively with chloroform, water, and acetone. Crude yield 280 g (76%).

While the phthalide (280 g) was boiled with a mixture of 700 cm³ of acetic acid and 450 cm³ of concd hydrochloric acid for 3 d, each 50 cm³ of concd hydrochloric acid was added to this solution at 10 h intervals (total 250 cm³). Phthalic acid deposited on cooling was filtered off and washed with water. The combined filtrate and washings were evaporated to near dryness under reduced pressure and the residue was treated with water to remove undissolved materials. The aqueous solution was again concentrated and a large amount of ethanol was added. The resulting precipitates were collected by filtration. Crude yield 135 g (96%).

The pure sample was obtained by repeated crystallization from dilute ethanol; mp 190–192 °C. IR: ν_{CO} 1720 cm⁻¹. Found: C, 31.52; H, 7.32; N, 14.79%. Calcd for C₆H₁₂N₂O·2HCl: C, 31.75; H, 7.46; N, 14.82%.

1,5-Diamino-3-pentanol dihydrochloride (Hdpl·2HCl): Crude 1,5-diamino-3-pentanone dihydrochloride (40 g, 0.21 mol) was added portionwise keeping the temperature below 20 °C to a solution containing sodium hydroxide (17 g, 0.4 mol) and sodium borohydride (8 g, 0.2 mol) in 300 cm³ water. The mixture was stirred at room temperature for 48 h. Dilute hydrochloric acid was carefully added to the cold solution and a pH was brought to ≈ 1 . The solution was evaporated to dryness under reduced pressure, and methanol was added

to the residue and evaporated. Addition of methanol and evaporation under reduced pressure was repeated several times to remove resulting boric acid as a methyl ester. The final residue was boiled with 100 cm³ of methanol, undissolved sodium chloride was filtered off, and the filtrate was concentrated to a small volume. A large amount of ether was added to the residual solution and the mixture was kept in a refrigerator overnight. The resulting crystals were collected and washed with ether. Crude yield 32 g (80%). They were recrystallized from methanol-ether mixture; mp 158–160 °C. Found: C, 31.35; H, 8.65; N, 14.57%. Calcd for C₆H₁₄N₂O·2HCl: C, 31.43; H, 8.45; N, 14.66%.

1,5-Bis(dimethylamino)-3-pentanol (Hmdpl):¹⁹⁾ A mixture of 1,5-bis(dimethylamino)-3-pentanone (30 g, 0.17 mol)²⁰⁾ and sodium borohydride (5 g, 0.13 mol) in 130 cm³ of methanol was heated at 60 °C for 1 h. It was poured on ice, acidified to pH 2–3 with concd hydrochloric acid, and the solution was evaporated to near dryness under reduced pressure. The residue was dissolved in a small amount of water, saturated with potassium hydroxide, and extracted with 300 cm³ of ether. The ether extracts were dried over potassium carbonate and the ether was evaporated. The oily residue was distilled and the fraction bp 115–116 °C (1800 Pa) was collected. Yield 20 g (70%). Found: C, 61.58; H, 12.71; N, 15.97%. Calcd for C₈H₂₂N₂O: C, 62.02; H, 12.72; N, 16.07%.

Cu₂(dpl)₂Cl₂·H₂O: To a solution of Hdpl·2HCl (1.9 g, 10 mmol) in 40 cm³ of methanol was added triethylamine until the solution became alkaline, and to this solution was added an equimolar amount of anhydrous copper(II) chloride in methanol. The resulting deep blue solution was heated on a water bath for a few minutes. On cooling to room temperature bluish violet crystals were separated and were recrystallized from a dilute methanol-water (1 : 1) mixture. Found: C, 26.58; H, 6.27; N, 12.23; Cu, 28.00%. Calcd for C₁₀H₂₈N₄O₃Cl₂Cu: C, 26.67; H, 6.27; N, 12.44; Cu, 28.22%.

The bromide, perchlorate, tetrafluoroborate, and nitrate were also prepared in similar manners using corresponding copper(II) salts and recrystallized from water containing sodium salt of the corresponding anion.

Cu₂(dpl)₂Br₂·H₂O: Found: C, 22.14; H, 5.28; N, 10.31%. Calcd for C₁₀H₂₈N₄O₃Br₂Cu₂: C, 22.27; H, 5.23; N, 10.39%.

Cu₂(dpl)₂(ClO₄)₂: Found: C, 21.48; H, 4.68; N, 9.80; Cu, 22.49%. Calcd for C₈H₁₃N₂O₆CuCl: C, 21.44; H, 4.68; N, 10.00; Cu, 22.68%.

Cu₂(dpl)₂(BF₄)₂: Found: C, 22.58; H, 4.95; N, 10.23; Cu, 23.52%. Calcd for C₈H₁₃N₂O₆CuBF₄: C, 22.45; H, 4.90; N, 10.45; Cu, 23.75%.

Cu₂(dpl)₂(NO₃)₂: Found: C, 24.75; H, 5.44; N, 17.23%. Calcd for C₈H₁₃N₅O₄Cu: C, 24.74; H, 5.40; N, 17.31%.

Cu₂Cl₂(OCH₃)(dpl)·CH₃OH: To a warm methanol solution (20 cm³) of Hdpl·2HCl (0.4 g, 2 mmol) was added trimethylamine to make the solution alkaline. Anhydrous copper(II) chloride (0.5 g, 4 mmol) dissolved in methanol was added to this solution and the mixture was heated on a water bath. Deep green crystals were soon separated out. They were collected by filtration, washed with methanol, and dried at room temperature under vacuum. The yield was almost quantitative. The complex is sparingly soluble in ordinary organic solvents and no further purification was carried out. Found: C, 22.44; H, 4.99; N, 7.51; Cu, 33.60; Cl, 18.48%. Calcd for C₇H₂₀N₂O₃Cl₂Cu₂: C, 22.23; H, 5.33; N, 7.41; Cu, 33.60; Cl, 18.75%.

Cu₂Br₂(dpl)·2CH₃OH: The procedure was the same as the above except for the use of anhydrous copper(II) bromide in place of the chloride. Olive green crystals, only slightly soluble in ordinary organic solvents. Found: C, 15.92; H, 3.68; N, 5.28%. Calcd for C₇H₂₁N₂O₃Br₂Cu₂: C, 15.34; H,

3.86; N, 5.11%.

Cu₂Cl₂(mdpl)OH: A solution of Hmdpl (0.4 g, 2.5 mmol) in 20 cm³ of methanol was mixed with anhydrous copper(II) chloride (0.7 g, 5 mmol) in methanol and the solution was made alkaline by the addition of excess trimethylamine. Green crystals were soon deposited on warming. They were collected by filtration and recrystallized from 1-butanol. Yield 0.8 g (90%). Found: C, 28.33; H, 5.55; N, 7.19; Cu, 33.23; Cl, 18.20%. Calcd for C₉H₂₂N₂O₂Cu₂Cl₂: C, 27.84; N, 5.71; N, 7.22; Cu, 33.73; Cl, 18.26%.

Cu₂Br₂(mdpl)OH: The synthetic procedure was the same as the above. Dark green fine needles were obtained by recrystallization from 1-butanol. Found: C, 22.27; H, 4.38; N, 5.67; Cu, 26.78; Br, 33.79%. Calcd for C₉H₂₂N₂O₂Cu₂Br₂: C, 22.65; H, 4.65; N, 5.87; Cu, 26.63; Br, 33.49%.

Ni₂(dpl)₂(Bph₄)₂(CH₃OH)₂: Nickel perchlorate hexahydrate (0.76 g, 2 mmol) and Hdpl·2HCl (0.4 g, 2 mmol) were dissolved in 15 cm³ of methanol. To this solution was added solid sodium hydroxide (0.25 g, 6 mmol). The green solution gradually changed into dark red yielding a white precipitate as the sodium hydroxide dissolved in the solution. The precipitate was filtered off, and to the filtrate was added an excess of sodium tetraphenylborate (about 1 g). Fine pink-red crystals were formed in the solution. These were filtered and washed with methanol. The crystals thus obtained were recrystallized from a methanol-DMF (10 : 1) solution by adding a methanol solution saturated with sodium tetraphenylborate (1 g). This compound is readily soluble in DMF, slightly soluble in methanol, and practically insoluble in water. Found: C, 68.21; H, 7.10; N, 5.45%. Calcd for C₃₀H₃₇N₄O₂-BNi: C, 68.36; H, 7.07; N, 5.31%.

Measurements. The electric conductivities of solutions were measured with a Yanagimoto Conductivity Outfit Model MY 7. Infrared and electronic spectra were recorded on a Hitachi 295 Infrared spectrophotometer and a Shimadzu MPS-5000 Spectrophotometer, respectively. Magnetic susceptibilities were measured by the Faraday method. The apparatus was calibrated by the use of [Ni(en)₃]S₂O₃.²¹⁾ The susceptibilities were corrected for the diamagnetism of the constituting atoms by the use of Pascal's constants.²²⁾ The effective magnetic moments μ_{eff} was calculated based on the equation $\mu_{\text{eff}} = 2.828\sqrt{(\chi_A - 60 \times 10^{-6})T}$.

Results and Discussion

1 : 1 Copper(II)-dpl Complexes. Cu₂(dpl)₂X₂H₂O (X = Cl, Br), Cu₂(dpl)₂Y₂ (Y = ClO₄, BF₄, NO₃): These complexes show subnormal magnetic moments at room temperature (Table 1). The temperature dependence of magnetic susceptibility was measured for the chloride, tetrafluoroborate and perchlorate, and the results were well simulated by the Bleaney-Bowers equation²³⁾ based on the assumption of binuclear structure with parameters, $2J = -640 \text{ cm}^{-1}$, $Na = 40 \times 10^{-6} \text{ cgs emu}$, $g = 2.1$ for the chloride and $2J = -965 \text{ cm}^{-1}$, $Na = 46 \times 10^{-6} \text{ cgs emu}$, $g = 2.1$ for the tetrafluoroborate, where J , Na , and g denote the general meanings. The perchlorate was practically diamagnetic in this temperature range. The binuclear structure was verified by the single-crystal X-ray structural analysis for Cu₂(dpl)₂Cl₂(H₂O)₃ which was obtained by recrystallization of Cu₂(dpl)₂-Cl₂H₂O from an aqueous solution. This compound consists of discrete binuclear units, where two dpl molecules and two copper atoms are roughly on a plane and a chloride ion and a water molecule weakly coor-

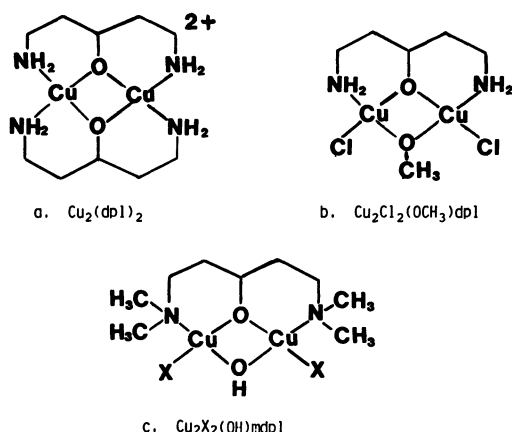
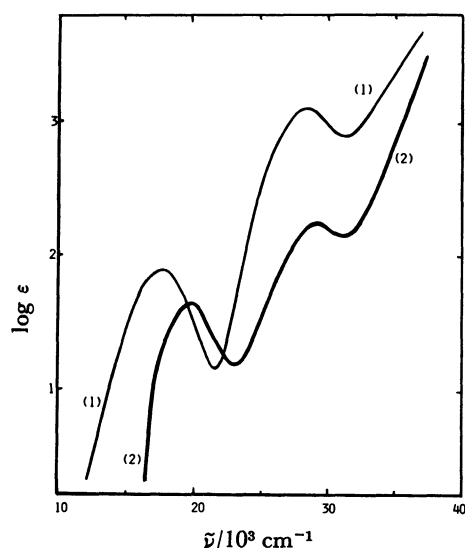


Fig. 1. Chemical structures of complexes.

Fig. 2. Electronic spectra of (1) $\text{Cu}_2(\text{dpl})_2(\text{BF}_4)_2$ in water (2) $\text{Ni}_2(\text{dpl})_2(\text{Bph}_4)_2 \cdot 2\text{CH}_3\text{OH}$ in methanol.

dinate to the copper ions from the same side of the coordination plane. The details of the structural data were reported in a separate paper.²⁴⁾

The measurements of molar conductivities (Table 1) revealed that the perchlorate and tetrafluoroborate are 1 : 2 electrolytes in methanol solution (10^{-3} mol dm^{-3}), whereas in the case of the chloride partial coordination of Cl^- is occurring in the methanol solution, since its conductivity is considerably lower than those of the former ones.

Aqueous solutions of these complexes gave the same

spectra (Fig. 2) irrespective of the counter anion, showing a d-d band at $17.7 \times 10^3 \text{ cm}^{-1}$ ($\epsilon = 76.6$) and a CT band at $28.4 \times 10^3 \text{ cm}^{-1}$ ($\epsilon = 1300$) which is characteristic of alkoxo-bridged copper(II) complexes. Since Beer's law is held for the aqueous solution, the complex ion, probably $[\text{Cu}_2(\text{dpl})_2(\text{H}_2\text{O})_4]^{2+}$, should be quite stable in aqueous solution. This is an important result, since no binuclear copper(II) complexes with alkoxide bridges which are stable in aqueous solution have been known so far.

2 : 1 Copper(II)-dpl Complexes. $\text{Cu}_2\text{Cl}_2(\text{dpl})(\text{OCH}_3)\text{CH}_3\text{OH}$: This compound shows subnormal magnetic moments at room temperature (0.89 BM) and the temperature dependence of magnetic susceptibility can be simulated by the Bleaney-Bowers equation²³⁾ with the parameters $-2J = 595 \text{ cm}^{-1}$, $g = 2.15$, $N\alpha = 60 \times 10^{-6}$ cgs emu in the range 130–300 K. The deviation from the theoretical curve in the low-temperature range (80–130 K) may be attributed to paramagnetic impurity, since recrystallization was not carried out due to the low solubility in any available solvents. From the above results we assume the binuclear structure as depicted in Fig. 1.

The Nujol mull spectrum shows two bands at 16.5 and $27.0 \times 10^3 \text{ cm}^{-1}$. The former is assigned to the d-d transition and the latter to the CT ($\text{O} \rightarrow \text{Cu}$) transition similarly to the case of the 1 : 1 complexes. The d-d band shifts to the lower energy side by $2.5 \times 10^3 \text{ cm}^{-1}$ relative to that of the $[\text{Cu}_2(\text{dpl})_2]\text{X}_2$ ($\text{X} = \text{ClO}_4$ and BF_4) as shown in Table 1. This is compatible with the proposed structure in Fig. 1, where chloride ions are substituted for amino groups as compared with the structure in Fig. 1-a.

This compound decomposes in water forming a blue solution with pale blue amorphous precipitates. When

TABLE 1. MOLAR CONDUCTIVITIES Λ ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ AT 25 °C, 10^{-3} mol dm^{-3}) AND EFFECTIVE MAGNETIC MOMENTS AT ROOM TEMPERATURE

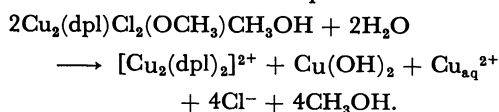
Complex	Λ	(Solvent)	μ_{eff} BM
$\text{Cu}_2(\text{dpl})_2\text{Cl}_2\text{H}_2\text{O}$	138	(Methanol)	0.72
$\text{Cu}_2(\text{dpl})_2(\text{BF}_4)_2$	184	(Methanol)	0.37
$\text{Cu}_2(\text{dpl})_2(\text{ClO}_4)_2$	172	(Methanol)	0.22
$\text{Cu}_2\text{Cl}_2(\text{mdpl})\text{OH}$	7.7	(DMF)	1.19
$\text{Cu}_2\text{Br}_2(\text{mdpl})\text{OH}$	7.3	(DMF)	1.55
$\text{Cu}_2\text{Cl}_2(\text{OCH}_3)(\text{dpl}) \cdot \text{CH}_3\text{OH}$			0.89
$\text{Ni}_2(\text{dpl})_2(\text{Bph}_4)_2 \cdot 2\text{CH}_3\text{OH}$	149	(Methanol)	0.72

TABLE 2. ELECTRONIC SPECTRAL DATA (cm^{-1} , ϵ IN PARENTHESIS)

Complex	Solution		(Solvent) ^{a)}	Nujol mull	
$\text{Cu}_2(\text{dpl})_2\text{Cl}_2\text{H}_2\text{O}$	17.7(76.6)	28.4(1300)	w	16.5(sh), 17.5	27
	18.0(59.0)	28.5(1400)	m		
$\text{Cu}_2(\text{dpl})_2(\text{BF}_4)_2$	18.0(57.0)	28.6(1520)	m	19.0	27
$\text{Cu}_2(\text{dpl})_2(\text{ClO}_4)_2$	18.0(56.5)	28.6(1610)	m	19.0	27
$\text{Cu}_2\text{Cl}_2(\text{dpl})\text{OCH}_3 \cdot \text{CH}_3\text{OH}$				16.5	27
$\text{Cu}_2\text{Cl}_2(\text{mdpl})\text{OH}$	14.1(175)	b)	DMF	15.0	26.0 ^{c)}
$\text{Cu}_2\text{Br}_2(\text{mdpl})\text{OH}$	13.9(273)	b)	DMF	14.0	23 ^{c)}
$\text{Ni}_2(\text{dpl})_2(\text{Bph}_4)_2 \cdot 2\text{CH}_3\text{OH}$	19.8(46)	29.8(160)	m	20.1	31 ^{c)}

a) w: Water, m: methanol. b) Obscure due to the overlapping of bands. c) Shoulder.

the solution was filtered and evaporated, well formed blue crystals of $\text{Cu}_2(\text{dpl})_2\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ separated out. Thus, the reaction that had taken place can be described as



Copper(II) Complexes with mdpl. $\text{Cu}_2\text{X}_2(\text{mdpl})\text{OH}$ ($\text{X}=\text{Cl}, \text{Br}$): All attempts to prepare the 1 : 1 complexes with mdpl similar to the dpl complexes were unsuccessful. This is most probably due to the steric repulsion between the methyl groups on the amine nitrogens. In contrast, the 2 : 1 complexes $\text{Cu}_2\text{X}_2(\text{mdpl})\text{OH}$ ($\text{X}=\text{Cl}, \text{Br}$) were readily obtained. The electric conductivities showed that both compounds are nonelectrolytes in DMF (*cf.* Table 1). This is consistent with the structure in Fig. 1.

Magnetic moments of these complexes at room temperature are both subnormal, *i.e.*, 1.19 BM ($\text{X}=\text{Cl}$) and 1.55 BM ($\text{X}=\text{Br}$) for one copper atom, but their magnetic behaviors over the temperature range 80–300 K are quite different from each other. As seen in Fig. 3 the χ_A -T curve of the chloro complex can be well simulated by the Bleaney-Bowers equation²³⁾ with $-2J=375\text{ cm}^{-1}$, $g=2.1$, and $N\alpha=60 \times 10^{-6}\text{ cgs emu}$. Thus, the binuclear structure as illustrated in Fig. 1 is assigned to the chloro complex. On the other hand, the χ_A -T curve of the bromo complex cannot be interpreted by the Bleaney-Bowers equation,²³⁾ but the χ_A^{-1} -T plots make a straight line in the range 110–300 K, giving a large Weiss constant -100 K (*cf.* Fig. 3). Such a magnetic behavior just corresponds to that of the group C-a according to the classification of Nishida

and Kida.⁷⁾

1 : 1 Nickel(II) Complex with dpl. $\text{Ni}_2(\text{dpl})_2(\text{Bph}_4)_2 \cdot 2\text{CH}_3\text{OH}$: The magnetic susceptibility of this compound is very low ($\chi_A=223 \times 10^{-6}\text{ cgs emu}$ at 294 K) and nearly constant in the range 80–300 K ($234 \times 10^{-6}\text{ cgs emu}$ at 80 K). This indicates that the compound is a spin-paired planar complex similar to the structure of Fig. 1-a, and the observed paramagnetism is due to the second-order Zeeman term.

The absorption spectrum in methanol is shown in Fig. 2. In the ultraviolet and visible region a single absorption band is observed at $19.8 \times 10^3\text{ cm}^{-1}$ ($\epsilon=46$), which is undoubtedly attributed to the d-d transitions. Such a spectral feature is consistent with the planar coordination of nickel(II) with an N_2O_2 donor set. The band at $28.9 \times 10^3\text{ cm}^{-1}$ ($\epsilon=160$), however, is not likely to be of a d-d origin, though the intensity is a reasonable one for a d-d band. Because, the red nickel(II) complex with a planar N_2O_2 donor set, such as bis(*N,N*-dimethylethylenediamine *N*-oxide)nickel(II) perchlorate, has only a single broad absorption band at $19.34 \times 10^3\text{ cm}^{-1}$ in the region of wavenumber lower than $30 \times 10^3\text{ cm}^{-1}$,²⁵⁾ furthermore, no d-d band has ever been reported for planar nickel(II) complexes in the region of wavenumber higher than $23 \times 10^3\text{ cm}^{-1}$.²⁶⁾ Therefore, this band is attributable to the charge transfer transition from the bridging oxygen to nickel, similarly to the bands at $28.6 \times 10^3\text{ cm}^{-1}$ observed for $[\text{Cu}_2(\text{dpl})_2]^{2+}$.

It is to be noted that a stable alkoxo-oxygen bridged planar nickel(II) complex has been first reported and characterized in this study, and it shows a band in the near-ultraviolet region whose origin seems to be similar to that of the bands characteristic of alkoxo-oxygen bridged copper(II) complexes.

No trials have been so far successful to isolate pure crystals of the complexes other than tetraphenylborate.

References

- 1) E. Uhlig and H. Schon, *Z. Anorg. Allg. Chem.*, **316**, 25 (1962).
- 2) E. Uhlig and K. Staiger, *Z. Anorg. Allg. Chem.*, **346**, 21 (1966).
- 3) Y. Ishimura, Y. Nonaka, Y. Nishida and S. Kida, *Bull. Chem. Soc. Jpn.*, **46**, 3728 (1973).
- 4) S. Kida, Y. Nishida and M. Sakamoto, *Bull. Chem. Soc. Jpn.*, **46**, 2428 (1973).
- 5) Y. Nishida and S. Kida, *Chem. Lett.*, **1974**, 339.
- 6) Y. Nishida, F. Numata, and S. Kida, *Inorg. Chim. Acta*, **11**, 189 (1974).
- 7) Y. Nishida and S. Kida, *J. Inorg. Nucl. Chem.*, **38**, 451 (1976).
- 8) R. Mergehenn and W. Haase, *Z. Naturforsch., Teil B*, **30**, 155 (1975).
- 9) N. Matsumoto, Y. Nishida, S. Kida, and I. Ueda, *Bull. Chem. Soc. Jpn.*, **49**, 177 (1976).
- 10) N. Matsumoto, Y. Nishida, I. Ueda, and S. Kida, *Bull. Chem. Soc. Jpn.*, **49**, 1308 (1976).
- 11) E. D. Este and D. J. Hodgson, *Inorg. Chem.*, **14**, 334 (1975).
- 12) W. Haase, *Chem. Ber.*, **106**, 3132 (1973).
- 13) R. Mergehenn, W. Haase, and R. Allmann, *Acta Crystallogr., Sect. B*, **31**, 1847 (1975).
- 14) N. Matsumoto, S. Kida, and I. Ueda, *J. Coord. Chem.*,

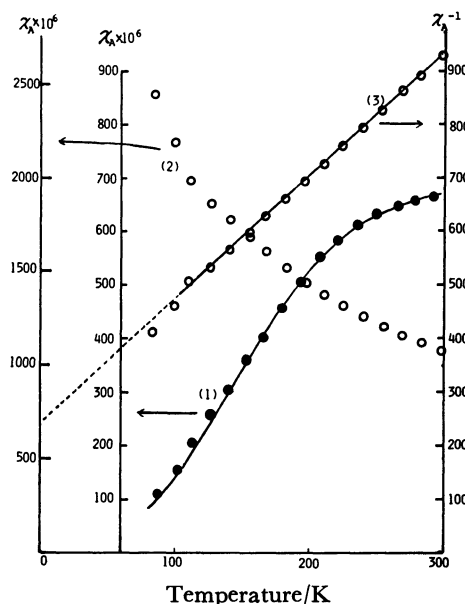


Fig. 3. Temperature dependence of magnetic susceptibilities, χ_A (cgs emu). (1) $\text{CuCl}_2(\text{mdpl})\text{OH}$: The second left side scale. The solid line is the theoretical curve based on the Bleaney-Bowers equation²³⁾ with the parameters, $2J=-375\text{ cm}^{-1}$, $g=2.1$, and $N\alpha=60 \times 10^{-6}\text{ cgs emu}$. (2) $\text{CuBr}_2(\text{mdpl})\text{OH}$: The first left side scale. (3) $\text{CuBr}_2(\text{mdpl})\text{OH}$: The right side scale (χ^{-1} -T plots).

9, 133 (1979).

15) R. Mergehenn, L. Merz, and W. Haase, *J. Chem. Soc., Dalton Trans.*, **1980**, 1703.

16) L. Merz and W. Haase, *J. Chem. Soc., Dalton Trans.*, **1980**, 875.

17) H. Taniyama and B. Yasui, *Yakugaku Zasshi*, **81**, 1497 (1961).

18) G. R. Owen and C. B. Reese, *J. Chem. Soc., C*, **1970**, 2401.

19) J. H. Biel, U. S. Patent 2937185; *Chem. Abstr.*, **54**, 18362 (1960).

20) N. Whittaker, *J. Chem. Soc.*, **1969**, 85.

21) N. F. Curtis, *J. Chem. Soc.*, **1961**, 3147.

22) P. W. Selwood, "Magnetochemistry," Interscience, New York (1956).

23) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

24) Y. Nishida and S. Kida, *Mem. Fac. Sci. Kyushu Univ., Ser. C*, **13**(1), 35 (1981).

25) S. Kida and T. Oniki, *Bull. Chem. Soc. Jpn.*, **45**, 1078 (1972).

26) Y. Nishida and S. Kida, *Coord. Chem. Rev.*, **27**, 275 (1979).