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Syntheses and Configurations of Copper(II) and Nickel(II) Complexes of *trans*-1,2-Dicyano-1,2-cyclohexanediamine

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Synopsis. Complexation of the solid and oily isomers of 1,2-dicyano-1,2-cyclohexanediamine (abbreviated as s-cychd and o-cychd respectively) with nickel(II) and copper(II) ions have been investigated. Only s-cychd formed the complexes Ni(s-cychd)$_2$Cl$_2$ and Cu(s-cychd)$_2$X$_2$ (X=Cl, Br, NO$_3$, ClO$_4$). Based on the configuration of the nickel complex, s-cychd was shown to be the (*E*)-isomer and thence o-cychd the (*Z*)-isomer. Configurations of the copper complexes have been dicussed on the basis of electronic spectra of DMF solution and of powder sample.

Recently we have shown that the Schiff bases derived from 1,2-bis(aminomethyl)-1,2-cyclohexanediamine and salicylaldehydes are novel binucleating ligands, which can form "strati-bis" metal complexes.[1,2] However, we have not yet determined if the geometrical structure of 1,2-bis(aminomethyl)-1,2-cyclohexanediamine is (*Z*) or (*E*); the amine having been prepared by reducing the solid form of two isomers (crystal melting at 170 °C and oily substance) of 1,2-dicyano-1,2-cyclohexanediamine. It is known that the *trans*-1,2-cyclohexanediamine differs from the *cis*-isomer in complexation with nickel(II) chloride.[3] Thus, in order to determine the geometrical structures of the solid and oily isomers of 1,2-dicyano-1,2-cyclohexanediamine (abbreviated as s-cychd and o-cychd respectively), we attempted to synthesize nickel(II) and copper(II) complexes of s-cychd and o-cychd and to examine their configurations.

Experimental

Preparations. *Ni(s-cychd)$_2$Cl$_2$*: A solution of s-cychd (0.50 g) and nickel(II) chloride hexahydrate (0.36 g) in ethanol (40 cm^3) was stirred at a temperature lower than 25 °C. Pale blue crystalline powder, which was deposited, was collected, washed with ethanol, and dried *in vacuo*.

Cu(s-cychd)$_2$X$_2$ (X=Cl, Br, NO$_3$, ClO$_4$). These complexes were obtained as purple to bluish purple crystalline powder by the reaction of s-cychd and a copper(II) salt in ethanol.

Elemental analyses of the complexes are given in Table 1.

Measurements. Electronic spectra were recorded on a Shimadzu MPS-5000 spectrometer in *N,N*-dimethylformamide (DMF) and on powder sample. Infrared spectra were recorded on a Hitachi 215 spectrometer on KBr disks. magnetic susceptibilities were measured by the Faraday method and magnetic moments were calculated by the equation, $\mu_{\mathrm{eff}}=2.828(\chi_{\mathrm{A}}\times T)^{1/2}$.

Results and Discussion

By the reaction of s-cychd with nickel(II) chloride hexahydrate, blue-colored Ni(s-cychd)$_2$Cl$_2$ was prepared. However, the reaction of s-cychd with nickel(II) bromide, nitrate or perchlorate afforded a white amorphous compound, which is free from nickel and practically insoluble in water and most organic solvents. Infrared spectrum of this compound reveals a band at 1640 cm^{-1} attributable to amide group. We presume that this compound is a self-condensation product of s-cychd. On the other hand, s-cychd reacted with copper(II) salts to form copper(II) complexes with chloride, bromide, nitrate, and perchlorate.

All the attempts to obtain a metal complex from o-cychd and a nickel(II) salt or a copper(II) salt were unsuccessful. Instead, a white amorphous compound was produced, which is supposed to be a self-condensation product of o-cychd.

Infrared spectrum of Ni(s-cychd)$_2$Cl$_2$ showed two CN stretching bands at 2240 and 2150 cm^{-1}, while the spectra of the copper complexes showed one band near 2300 cm^{-1}. Nitrate and perchlorate ions are not coordinated to the metal in the copper complexes

Table 2. Magnetic moments and spectral data of complexes

	μ_{eff}/BM (T/K)	d-d and CT/10^3 cm^{-1}		
		Absorption in DMF (ε/mol^{-1} dm^3 cm^{-1})		Reflectance
Ni(s-cychd)$_2$Cl$_2$	3.07 (286.1)	8.9 (5.1)	14.7 (6 2)	9.1 15.2
		16.0 (5.5)	24.3 (14.6)	16.1 25.0
Cu(s-cychd)$_2$Cl$_2$	1.83 (288.6)	14.1 (69)	22.9 (216)	15.6
Cu(s-cychd)$_2$Br$_2$	1.83 (288.5)	14.0 (143)	22.2 (86)	16.0
Cu(s-cychd)$_2$-(NO$_3$)$_2$	1.84 (290.5)	14.6 (24)		17.9
Cu(s-cychd)$_2$-(ClO$_4$)$_2$	1.76 (287.0)	14.6 (53)		17.5

Concentratiosn of the solutions are *ca.* 1 × 10^{-3} mol dm^{-3}.

Table 1. Elemental analyses of complexes

	Found(%)				Calcd (%)			
	C	H	N	M	C	H	N	M
Ni(s-cychd)$_2$Cl$_2\cdot$1/2H$_2$O	41.44	5.32	24.00	11.95	41.15	5.40	23.99	12.57
Cu(s-cychd)$_2$Cl$_2$	41.29	5.30	23.94	13.70	41.52	5.23	24.21	13.73
Cu(s-cychd)$_2$Br$_2\cdot$1/2H$_2$O	34.44	4.37	19.98	10.81	34.26	4.49	19.98	11.33
Cu(s-cychd)$_2$(NO$_3$)$_2\cdot$C$_2$H$_5$OH	38.33	5.37	25.25	11.26	38.47	5.38	24.92	11.31
Cu(s-cychd)$_2$(ClO$_4$)$_2\cdot$1/2H$_2$O	32.26	4.20	18.34	10.74	32.04	4.20	18.68	10.59

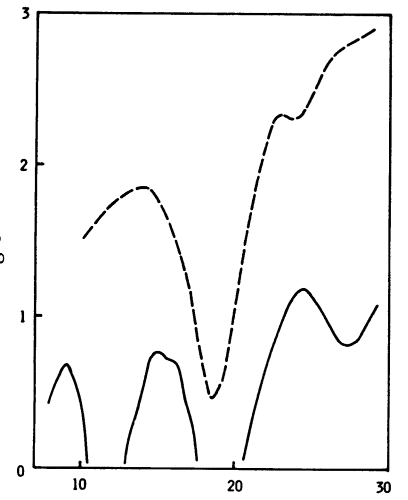

Fig. 1. Electronic spectra of (——) $Ni(s\text{-}cychd)_2Cl_2$ and (------) $Cu(s\text{-}cychd)_2Cl_2$.

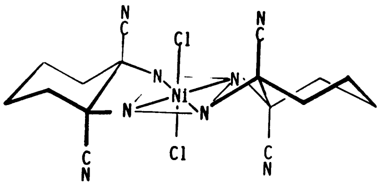

Fig. 2. Possible structure of $Ni(s\text{-}cychd)_2Cl_2$.

judging from their ν(NO) and ν(ClO) bands (NO_3^- 1360; ClO_4^- 1100 cm^{-1}).[4]

Magnetic moments and band frequencies of electronic spectra are given in Table 2. The electronic spectra of $Ni(s\text{-}cychd)_2Cl_2$ and $Cu(s\text{-}cychd)_2Cl_2$ in DMF are shown in Fig. 1. Electronic spectra of the nickel complex in DMF and on powder clearly indicate that the geometry around the metal is essentially octahedral. Splitting of the band $^3T_{1g} \leftarrow {}^3A_{2g}$ into two components may be attributed to the lowering of symmetry. The magnetic moment of this complex is quite normal for an octahedral nickel(II) complex.

Saito and Kidani[3] have shown that *trans*-1,2-cyclohexanediamine forms an octahedral nickel(II) complex, while the *cis*-isomer forms a planar complex. Hence, isolation of octahedral $Ni(s\text{-}cychd)_2Cl_2$ indicates that s-cychd is of the (*E*)-form. Thus, we may conclude that o-cychd is of the (*Z*)-form. A plausible structure of the nickel complex is shown in Fig. 2. The amino groups of s-cychd are equatorial when s-cychd coordinates to a metal and hence cyano groups are axial. Judging from the orientation of the cyano groups in $Ni(s\text{-}cychd)_2Cl_2$, it seems that there is little steric hinderance between the cyano groups and the chloride ion coordinated at the apical position.

Reflectance spectra of the copper complexes showed a broad band around (15—18) × 10^3 cm^{-1} attributable to the d-d band. Relatively high frequencies of the bands for the nitrate and perchlorate complexes indicate the planar configuration around the metal ion, being consistent with the infrared spectral data implying non-coordination of the anions. On the other hand, the coordination geometry of the chloride and bromide copper complexes was assumed to be of a five-coordination with a halide ion at the apical position. Absorption spectra of all the copper complexes in DMF showed d-d band centered at (14—15) × 10^3 cm^{-1}. This suggests that an anion or a solvent molecule coordinates to the metal to form a five- or six-coordinate configuration in DMF. Notably, the spectra of the complexes with halide ions in DMF showed an additional band at (22—23) × 10^3 cm^{-1}, which was not clearly recognized in the reflectance spectra owing to the poor resolution. It seems reasonable to assign this band to the CT transition from halide ion to copper(II) ion. The molar extinction coefficient (ε) of the band of $Cu(s\text{-}cychd)_2Cl_2$ was practically independent of the concentration examined in this study (3.36×10^{-3}–1.03×10^{-4} mol dm^{-3}). On the other hand, that of the band of $Cu(s\text{-}cychd)_2Br_2$ was remarkably dependent on the concentration; ε decreased upon dilution and the band almost disappeared at the concentration 9.05×10^{-5} mol dm^{-3}. Thus, it is likely that the bromide ion is readily replaced by the solvent molecule in DMF.

References

1) T. Izumitani, M. Nakamura, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **55**, 2122 (1982).

2) T. Izumitani, H. Ōkawa, and S. Kida, *Chem. Lett.*, **1981**, 483..

3) R. Saito and Y. Kidani, *Chem. Lett.*, **1976**, 123.

4) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York (1970), pp. 98, 111.