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Copper and Nickel Complexes of Meso and Racemic 2, 3-Diaminosuccinic Acids[*1]

YUZO YOSHIKAWA and KAZUO YAMASAKI

Inorganic Chemistry Laboratory, Faculty of Science, Nagoya University, Chikusa, Nagoya

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The 1 : 1 and 1 : 2 complexes of copper and nickel with meso and racemic 2, 3-diaminosuccinic acids were prepared, and their structures were studied by determining their magnetic moments and absorption and reflectance spectra. The 1 : 2 complexes have the following chemical compositions: $Na_2[Cu(m\text{-}das)_2]\cdot 8H_2O$, $Na_2[Cu(r\text{-}das)_2]\cdot 7^1/_2H_2O$, $Na_2[Ni(m\text{-}das)_2]\cdot 4^1/_2H_2O$ and $Na_2[Ni(r\text{-}das)_2]\cdot 7H_2O$, where "das" indicates a diaminosuccinate ion. In these complexes the ligand seems to be coordinated with the amino groups. The 1 : 1 complexes of both copper and nickel are coordination polymers. The reflectance spectra suggest that Cu(m-das) might have a trans(N) and Cu(r-das), a cis(N) configuration.

The metal complexes of 2, 3-diaminosuccinic acid have scarcely been studied at all; only a copper complex was reported on in 1893.[1] This ligand has two asymmetric carbon atoms, and there exist meso and racemic forms, just as with tartaric acid. It would, therefore, be interesting to study the complexes of this ligand since this is a quadridentate ligand with a structure resembling both ethylenediamine and glycine, and it may form coordination polymers with metals. In the present study copper and nickel complexes of the meso and racemic forms of 2, 3-diaminosuccinic acid were prepared and their properties were studied. Both copper and nickel form, with this ligand, complexes with metal-to-ligand ratios of 1 : 1 and 1 : 2, the former being coordination polymers. The properties of the meso and racemic complexes are almost the same except for the 1 : 1 complexes of copper. In this article the abbreviations "m-dasH$_2$" and "r-dasH$_2$" will be used for the meso and racemic forms of 2, 3-diaminosuccinic acid respectively.

Experimental

Materials. Meso and racemic diaminosuccinic acids were prepared from sodium dihydroxytartrate by the method of Farchy and Tafel.[1] The meso acid melts at 209—210°C (decomp.).

Found: N, 18.94%. Calcd for $C_4H_8N_2O_4$: N, 18.91%.

The racemic acid melts at 214—215°C (decomp.).

Found: N, 18.89%. Calcd for $C_4H_8N_2O_4$: N, 18.91%.

Both acids are soluble in water only with difficulty due to the formation of zwitter ions, as is indicated by the absence of the infrared absorption band characteristic of –COOH groups at about 1700 cm^{-1}.

(1) Sodium Bis(m-diaminosuccinato)cuprate(II), $Na_2[Cu(m\text{-}das)_2]\cdot 8H_2O$. To 1 g of meso diaminosuccinic acid dissolved in 15 m*l* of 1 N NaOH, 0.5 g of $CuCl_2\cdot 2H_2O$ dissolved in 5 m*l* of water was added. The violet solution thus obtained was filtered, and violet needle crystals were precipitated by adding ethyl alcohol. The crystals were then reprecipitated from water by adding ethyl alcohol; the crystals obtained were washed with 50% ethyl alcohol and dried at room temperature. This complex is readily soluble in water, but the solution is unstable, and upon standing it decomposes into the ligand and the 1 : 1 copper complex. The water of crystallization was completely lost upon heating at 100°C *in vacuo* for 3 hr.

Found: Cu, 11.63; N, 10.33; H$_2$O, 26.49%. Calcd for $Na_2CuC_8H_{12}N_4O_8\cdot 8H_2O$: Cu, 11.64; N, 10.26; H$_2$O, 26.59%.

(2) Sodium Bis(r-diaminosuccinato)cuprate(II), $Na_2[Cu(r\text{-}das)_2]\cdot 7\frac{1}{2}H_2O$. This complex was prepared in the same way as the complex 1.

Found: Cu, 11.86; N, 10.30; H$_2$O, 25.28%. Calcd for $Na_2CuC_8H_{12}N_4O_8\cdot 7\frac{1}{2}H_2O$: Cu, 11.84; N, 10.44; H$_2$O, 25.17%.

(3) m-Diaminosuccinatocopper(II), Cu(m-das)·1—2H$_2$O. To 1 g of sodium bis(m-diaminosuccinato)-cuprate(II) dissolved in 40 m*l* of water, an equimoleculan

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[1] J. N. Farchy and J. Tafel, *Ber.*, **26**, 1980 (1893).

amount of copper(II) chloride was added. From the mixture this complex is immediately precipitated because it is insoluble in water and organic solvents. It is a blue powder. The amount of water of crystallization is not definite, but is about 1—2 mol. When the complex is heated at 78°C *in vacuo* for 3 hr, the water of crystallization is completely lost.

Found for the anhydrous complex: Cu, 30.94; N, 12.46%. Calcd for $CuC_4H_6N_2O_4$: Cu, 30.31; N, 13.36%.

(4) r-Diaminosuccinatocopper(II), Cu(r-das)·1-2H_2O. This complex was prepared in the same way as the complex 3. It is a deep blue powder insoluble in water. The amount of water of crystallization is not definite, but is about 1—2 mol.

Found for the anhydrous complex: Cu, 30.31; N, 13.08%. Calcd for $CuC_4H_6N_2O_4$: Cu, 30.31; N, 13.36%.

(5) Sodium Bis(m-diaminosuccinato)niccolate(II), Na_2-[Ni(m-das)$_2$]·4½H_2O. This complex was prepared in a way similar to that used for the corresponding copper complex, using nickel chloride instead of copper chloride. Frequently the complex did not crystallize immediately and a blue syrup was obtained which gave small violet needles after having been warmed gently. This complex is readily soluble in water, and the aqueous solution is stable, unlike the corresponding copper complex. The water of crystallization is lost when the complex is heated at 153°C *in vacuo* for 5 hr.

Found: Ni, 12.27; N, 12.83; H_2O, 17.32%. Calcd for $Na_2NiC_8H_{12}N_4O_8$·4½H_2O: Ni, 12.28; N, 12.94; H_2O, 16.96%.

(6) Sodium Bis(r-diaminosuccinato)niccolate(II), Na_2-[Ni(r-das)$_2$]·7H_2O. This complex was prepared in the same way as the complex 5. It is a violet needle.

Found: Ni, 11.17; N, 10.84; H_2O, 23.86%. Calcd for $Na_2NiC_8H_{12}N_4O_8\cdot 7H_2O$: Ni, 11.23; N, 10.71; H_2O, 24.11%.

(7) m-Diaminosuccinatonickel(II), Ni(m-das)·3-4H_2O. This complex was prepared in a way similar to that used for the corresponding copper complex 3. It is a pale blue powder slightly soluble in water. The amount of water of crystallization is not definite, but is 3—4 moles. The water of crystallization is lost when the complex is heated at 153°C *in vacuo* for 5 hr.

Found for the anhydrous complex: Ni, 28.57; N, 13.41%. Calcd for $NiC_4H_6N_2O_4$: Ni, 28.66; N, 13.68%.

(8) r-Diaminosuccinatonickel(II), Ni(r-das)·3-4H_2O. This complex was prepared in the same way as the complex 7. It is a pale blue powder slightly soluble in water.

Found for the anhydrous complex: Ni, 28.87; N, 13.12%. Calcd for $NiC_4H_6N_2O_4$: Ni, 28.66; N, 13.68%.

Measurements. The ultraviolet, visible, and near infrared absorption spectra of aqueous solutions of the complexes were determined by means of a Hitachi EPU-2A spectrophotometer, using quartz cells with thicknesses of 10 and 50 mm. Diffuse reflectance spectra of the powdered complexes passing through a 200-mesh sieve were determined by the above spectrophotometer equipped with a diffuse reflectance attachment, using magnesium oxide as the reference.

The magnetic moments of the complexes were determined by the Gouy method at room temperature, 23—28°C. The molar susceptibilities so obtained were then corrected for the diamagnetism of cations and the ligands. The X-ray powder diffraction patterns of the complexes were taken with a NORELCO X-ray diffractometer, using Cu$K\alpha$ radiation.

Results and Discussion

The 1 : 2 Complexes of Copper and Nickel.

The absorption spectra of aqueous solutions of the 1 : 2 complexes of copper and nickel are shown in Figs. 1 and 2; the data are given in Table 1, together with those of the ethylenediamine and glycine

TABLE 1

Complex	Absorption spectra ($\times 10^{-13}$ sec^{-1})			Magnetic moment	
	ν_{max} (log ε)	ν_{max} (log ε)	ν_{max} (log ε)	Obs.	Calcd.
Na_2[Cu(m-das)$_2$]	53.0 (1.74) *50.1 (1.65)			1.88 B. M.	1.73 B. M. for one unpaired electron
Na_2[Cu(r-das)$_2$]	52.8 (1.74) *50.2 (1.65)			1.90	
Cu(m-das)	*49.7 (1.64)			1.87	
Cu(r-das)	*49.9 (1.63)			1.93	
[Cu(en)$_2$]$^{2+}$	54.0 (1.85)				
Na_2[Ni(m-das)$_2$]	32.3 (0.83)	54.2 (0.67)	86.5 (0.76)	3.11	2.83 B. M. for two unpaired electrons
Na_2[Ni(r-das)$_2$]	31.9 (0.86)	53.9 (0.66)	86.0 (0.74)	3.13	
Ni(m-das)	29.1 (0.95)	48.9 (0.60)	80.4 (0.85)	3.33	
Ni(r-das)	29.0 (0.94)	48.1 (0.59)	80.0 (0.84)	3.36	
[Ni(H_2O)$_4$ en]$^{2+}$ **	30.8 (0.68)	48.5 (0.54)	81.0 (0.76)		
[Ni(H_2O)$_2$(en)$_2$]$^{2+}$ **	31.9 (0.81)	52.5 (0.71)	84.0 (0.87)		
[Ni(H_2O)$_2$(gly)$_2$]^0 **	29.3 (0.85)	48.8 (0.68)	80.8 (0.90)		

* These spectra were determined in 1 N NaOH.

** The data were taken from H. Ito, *Nippon Kagaku Zassi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **77**, 1383 (1956).

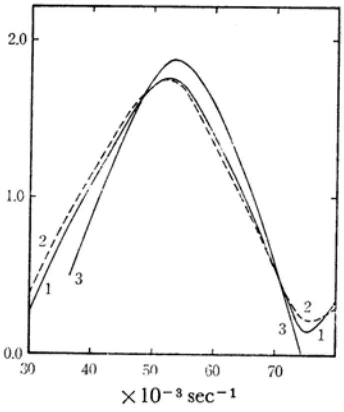

Fig. 1. Absorption spectra of the 1 : 2 copper complexes.

1: $Na_2[Cu(r\text{-}das)_2]$, 6×10^{-3} M
2: $Na_2[Cu(m\text{-}das)_2]$, 6×10^{-3} M
3: $[Cu(en)_2]^{2+}$

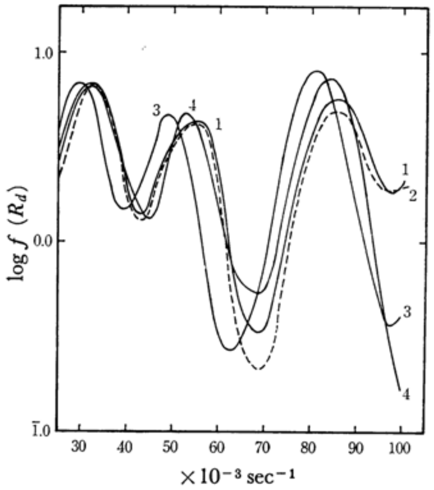

Fig. 2. Absorption spectra of the 1 : 2 nickel complexes.

1: $Na_2[Ni(r\text{-}das)_2]$, 3×10^{-2} M
2: $Na_2[Ni(m\text{-}das)_2]$, 4×10^{-2} M
3: $[Ni(H_2O)_2(gly)_2]^0$, 10^{-1} M
4: $[Ni(H_2O)_2(en)_2]^{2+}$, 2.5×10^{-1} M

complexes of the corresponding metals. The absorption spectra of meso and racemic diaminosuccinic acid complexes are similar to those of bis-ethylenediamine complexes. This may suggest a similarity in their structures: that is, in these 1 : 2 complexes the ligands seem to be coordinated to copper or nickel with their amino groups. The 1 : 2 complexes of nickel are stable in water, while those of copper slowly decompose and a mixture of the ligand and the 1 : 1 copper complex is precipitated, which has been identified by X-ray diffraction. The decomposition of the copper complexes seems to be facilitated by the insolubility of the 1 : 1 complexes for which no absorption spectra were available; their polymeric structures are suggested by X-ray diffraction.

When these 1 : 2 complexes of copper are dissolved in 1 N NaOH, the absorption bands of the solutions are at longer wavelengths than those in water, as may be seen in Table 1, indicating a possible replacement of the ligand molecule by OH groups. By the further addition of the ligand to the solution in alkali, the absorption bands shift to shorter wavelengths; the curve coincides with that of the original 1 : 2 complex in water (Fig. 1) when fifty times as much ligand as copper is added to the solution. The structures of copper complexes existing in alkali solutions have been studied by several workers, and the formation of five-coordinated $[Cu(OH)(en)_2]^+$ and four-coordinated $[Cu(OH)_2(R_2\text{-}en)]^0$ and $[Cu(OH)_2dip]^0$ from

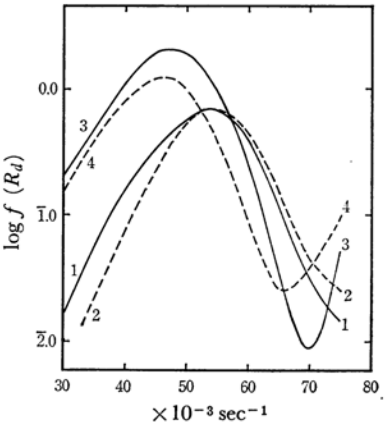

Fig. 3. Reflectance spectra of the copper complexes.

1: $Na_2[Cu(r\text{-}das)_2]$ 2: $Na_2[Cu(m\text{-}das)_2]$
3: Cu(r-das) 4: Cu(m-das)

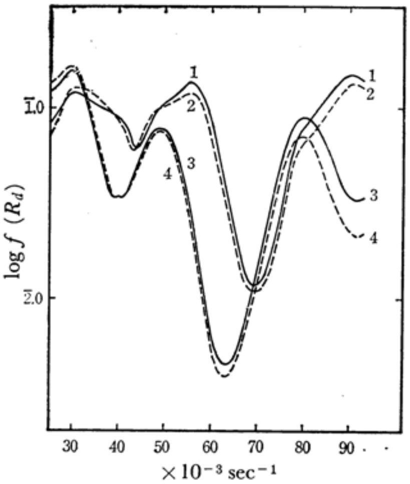

Fig. 4. Reflectance spectra of the nickel complexes.

1: $Na_2[Ni(r\text{-}das)_2]$ 2: $Na_2[Ni(m\text{-}das)_2]$
3: Ni(r-das) 4: Ni(m-das)

$[Cu(en)_2]^{2+}$, $[Cu(R_2\text{-}en)_2]^{2+}$ and $[Cu(dip)_n]$,$^{2+}$ $n=1$—3 has been reported by Jonassen *et al.*,²⁾ Ojima and Sone,³⁾ and Ojima⁴⁾ respectively. Therefore, the first complex formed by dissolving the 1 : 2 complexes in 1 N NaOH is presumed to be $[Cu(OH)_2das]^{2-}$; it becomes $[Cu(das)_2]^{2-}$ when an excess amount of the ligand is added.

The diffuse reflectance spectra in the solid state are the same for meso and racemic diaminosuccinic acid complexes of the respective metals (Figs. 3 and 4). The magnetic moments observed are all normal, indicating no direct interaction between metal atoms in these complexes (Table 1).

From the above facts, it may be concluded that the ligands in these 1 : 2 complexes of copper and nickel are coordinated by the amino groups, forming 4 N-type complexes like $[Cu(en)_2]^{2+}$.

The 1 : 1 Complexes of Copper and Nickel. The 1 : 1 complexes of nickel are completely amorphous, not showing any X-ray diffraction pattern, while those of copper show rather broad peaks with reproducible profiles. Therefore, the 1 : 1 complexes of both metals seem to have polymeric structures, the ligands linking metal atoms, but the normal values of the magnetic moments observed exclude the possibility of the direct interaction of metal atoms, as in a dimeric structure. The insolubility of the copper complexes and the slight solubility of the nickel complexes in water also support the polymeric structures.

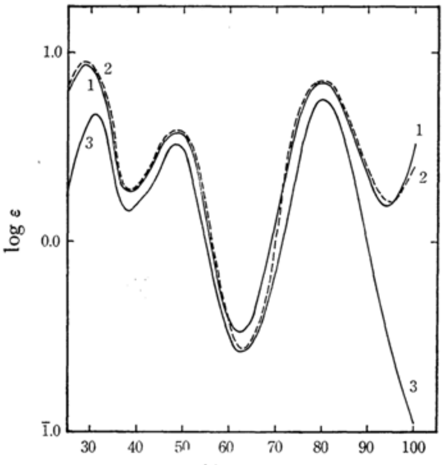

Fig. 5. Absorption spectra of the 1 : 1 nickel complexes.
1: Ni(r-das), 5×10^{-3} M
2: Ni(m-das), 3×10^{-3} M
3: $[Ni(H_2O)_4(en)]^{2+}$, 2.5×10^{-1} M

Although the 1 : 1 complexes of nickel are polymeric in the solid state, they are slightly soluble in water; in Fig. 5 their absorption spectra are shown, together with those of the ethylenediamine-nickel complex. The solubility of these 1 : 1 nickel complexes in water suggests their depolymerization into monomers which show absorption spectra similar to those of the monoethylenediamine-nickel complex. Therefore, in these monomers coordination with the 2 N, 4O type, as in $[Ni(H_2O)_4(en)]$,$^{2+}$ is most probable.

Since the 1 : 1 complexes of copper are soluble only in alkali, their absorption spectra were determined in 1 N NaOH solution. The absorption bands are listed in Table 1. In 1 N NaOH the 1 : 1 complexes show the same spectra as the 1 : 2 complexes; their bands shift to shorter wavelengths upon the further addition of the ligands, until finally the curves coincide with those of the 1 : 2 complexes in water, as has been discussed above.

The diffuse reflectance spectra of the meso and racemic diaminosuccinic acid complexes are the same for nickel, while they are slightly different for copper, as shown in Fig. 3, indicating some different structures in the solid state. Yasui and Shimura⁵⁾ studied the reflectance spectra of copper complexes of amino acids and reported that complexes with the cis(N) configuration of the ligands always had more intense bands than those with the trans(N) configuration. If this relationship holds also for the 1 : 1 complexes of diaminosuccinic acid with copper, the racemic acid complex may have the cis(N), and the meso acid complex, the trans(N), configurations of the ligand respectively, since the former has a more intense band than the latter. Therefore, the possible structures of these polymeric

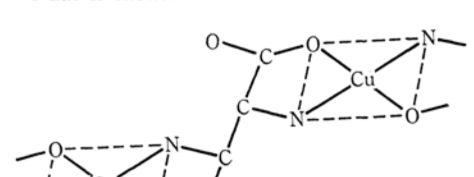

Fig. 6a. Polymeric structure suggested for Cu(r-das). In the figure only one form of r-das is shown.

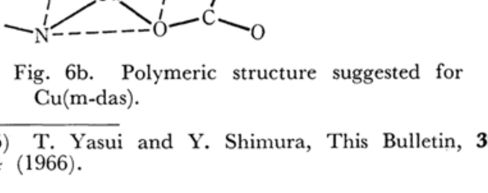

Fig. 6b. Polymeric structure suggested for Cu(m-das).

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2) H. B. Jonassen, R. E. Reeves and L. Segal, *J. Am. Chem. Soc.*, **77**, 2748 (1955).

3) H. Ojima and K. Sone, This Bulletin, **35**, 298 (1962).

4) H. Ojima, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **84**, 787 (1963).

5) T. Yasui and Y. Shimura, This Bulletin, **39**, 604 (1966).

1 : 1 copper complexes may be presumed to be composed of long chains, as is shown in Fig. 6. The possibilities of the cis(N) configuration for the meso acid complex and the trans(N) configuration for the racemic acid complex may be excluded, because of the steric hindrance. For the completely amorphous nickel complexes, very little information about their structures is available, although they seem to be composed of polymeric chains similar to those of copper complexes. The indefinite amounts of water of crystallization for the 1 : 1 complexes of copper and nickel seem to be related to their polymeric structures.

Coordination polymers have been studied by various workers, and those of bis(amino acids) type have been reported to be insoluble precipitates.⁶⁾ Hawkins and Perrin⁷⁾ studied polynuclear complex formation between copper ion and 2, 7-diaminosuberic acid, and determined the stability constants of mononuclear and polynuclear complexes formed in solution. These study was made possible because the ligand was soluble in water, however in the present study the ligand itself was insoluble. They also prepared an insoluble dimeric complex, di-μ-(2, 7-diaminosuberato)-dicopper(II), which had a metal-to-ligand ratio of 1 : 1. This dimeric complex corresponds to the 1 : 1 complexes in the present study, although the degrees of polymerization of the latter are not known.

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6) J. R. Elliott, Thesis, University of Illinois (1943). Cited in F. G. A. Stone and W. A. G. Graham, eds., "Inorganic Polymers," Academic Press, New York (1962), p. 510.

7) C. J. Hawkins and D. D. Perrin, *Inorg. Chem.*, **2**, 839 (1963).