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Binuclear Metal Complexes. XV.[1] Copper(II) and Nickel(II) Complexes of Binucleating Ligands Derived From 3-Formylsalicylic Acid and Diamines[2]

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Copper(II) and nickel(II) complexes of the 3-formylsalicylic acid–diamine Schiff bases, H_4fsaen, H_4fsapn, H_4fsatn, H_4fsaph, and H_4fsach, where en, pn, tn, ph, and ch denote ethylenediamine, propylenediamine, trimethylenediamine, *o*-phenylenediamine, and 1,2-cyclohexanediamine respectively, have been obtained and characterized. Binuclear copper(II) complexes, Cu_2(fsaen)·$2H_2O$, Cu_2(fsapn)·$2H_2O$, Cu_2(fsatn)·$2H_2O$, Cu_2(fsaph)·H_2O, and Cu_2(fsach)·$2H_2O$, show a strong antiferromagnetic spin-exchange interaction between metal ions, $-2J$ values being more than 555 cm^{-1}. It was revealed that Ni_2(fsaen)·$3H_2O$, Ni_2(fsapn)·$3H_2O$, Ni_2(fsaph)·$5H_2O$, and Ni_2(fsach)·$3H_2O$ are novel binuclear complexes composed of one paramagnetic and one diamagnetic nickel(II) ions. On the other hand, Ni_2(fsatn)·$5H_2O$ is a binuclear complex of paramagnetic nickel(II) ions. Its magnetism obeys the Curie-Weiss law in the range from liquid nitrogen temperature to room temperature with the Weiss constant of −40 K.

In the previous papers of this series,[3,4] we have reported that 3-formylsalicylic acid and its Schiff bases with alkyl amines form binuclear copper(II) and nickel(II) complexes. In those complexes the phenolic oxygen operates as a bridging group, and the carboxylate oxygen and the formyl oxygen or imino nitrogen coordinate to metal ion. It is supposed that two organic moieties are constructed *trans* to each other (Fig. 1).

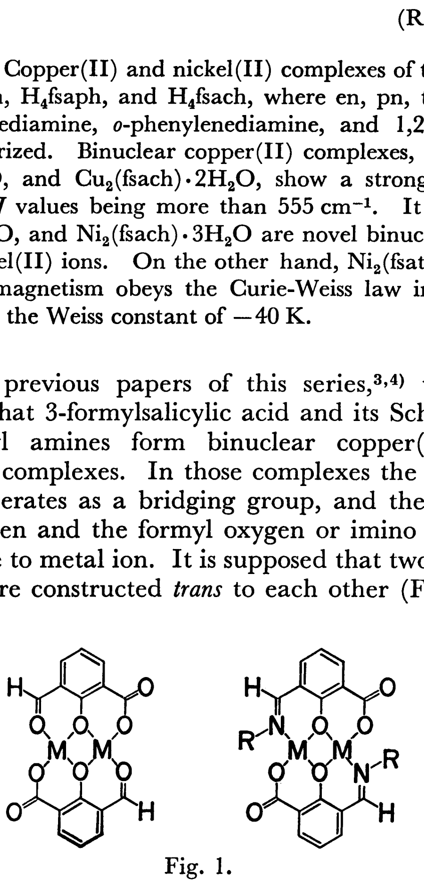

Fig. 1.

The Schiff bases derived from 3-formylsalicylic acid and diamines would form binuclear complexes bridged by the phenolic oxygens. One of the purposes of this study is synthesizing binuclear copper(II) complexes with these Schiff bases and investigating the spin-spin exchange interaction between copper(II) ions.

Geometrical requirement of the ligands results in the formation of a *cis*-configuration complex with respect to the imino nitrogens and the carboxylate oxygens. Therefore, the "inside" coordination site has N_2O_2-coordinating atoms, while the "outside" coordination site has O_4-coordinating atoms. Since there is a considerable difference in the ligand field strength between the "inside" and "outside" coordination spheres, the present ligands might form a binuclear nickel(II) complex composed of one paramagnetic and one diamagnetic metal ions. Synthesis of the binuclear nickel(II) complex of a novel spin-state is another purpose of this study.

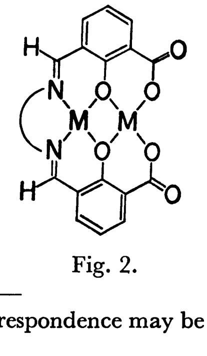

Fig. 2.

The 3-formylsalicylic acid-diamine Schiff bases utilized in this study are as follows: H_4 fsaen (Schiff base with ethylenediamine), H_4fsapn (propylenediamine), H_4fsatn (trimethylenediamine), H_4fsaph (*o*-phenylenediamine), and H_4fsach (1,2-cyclohexanediamine). The binuclear copper(II) and nickel(II) complexes with these ligands were synthesized and characterized on the basis of elemental analyses, infrared spectra, visible spectra, and magnetic measurements. The binuclear complexes are abbreviated as Cu_2(fsaen), Ni_2(fsapn), and so on. The mononuclear complexes, M(H_2fsaen)·1/$2H_2O$ and M(H_2fsapn)·1/$2H_2O$ (M=Cu(II) and Ni(II)), were also isolated and characterized.

Experimental

Syntheses. 3-Formylsalicylic acid was prepared after the method of Duff and Bills.[5] The synthetic procedures of the complexes are the same in principle. Syntheses of Cu(H_2fsaen)·1/$2H_2O$, Cu_2(fsaen)·$2H_2O$, and Ni_2(fsaen)·$3H_2O$ are represented.

Cu_2(H_2fsaen)·1/$2H_2O$. 3-Formylsalicylic acid (136 mg) was dissolved in an aqueous solution (30 ml) of sodium carbonate (55 mg), and then ethylenediamine (30 mg) was added. To this hot solution was added an aqueous solution (10 ml) of copper(II) acetate monohydrate (100 mg). Soon purple needles separated. After the reaction mixture was warmed at 60°C for a while, the product was isolated, washed with hot water and dried under reduced pressure.

Cu_2(fsaen)·$2H_2O$. An aqueous solution (30 ml) containing 3-formylsalicylic acid (136 mg), ethylenediamine (30 mg) and sodium carbonate (55 mg) was warmed at *ca.* 60°C

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TABLE 1. ELEMENTAL ANALYSES OF COMPLEXES

Complex[a]	Found (%) C	H	N	M	Calcd (%) C	H	N	M
$Cu(H_2fsaen)\cdot 1/2H_2O$	50.85	3.38	6.65	14.92	50.65	3.54	6.56	14.89
$Cu(H_2fsapn)\cdot 1/2H_2O$	52.00	3.67	6.37	14.71	51.76	3.89	6.35	14.41
$Ni(H_2fsaen)\cdot 1/2H_2O$	51.45	3.52	6.89	13.57	51.22	3.58	6.64	13.91
$Ni(H_2fsapn)\cdot 1/2H_2O$	52.18	4.36	6.22	13.11	52.33	3.98	6.42	13.46
$Cu_2(fsaen)\cdot 2H_2O$	41.28	3.07	5.15	24.60	41.95	3.13	5.44	24.66
$Cu_2(fsapn)\cdot 2H_2O$	42.80	3.43	5.28	24.33	43.10	3.43	5.29	24.00
$Cu_2(fsatn)\cdot 2H_2O$	42.86	3.45	5.29	23.92	43.10	3.43	5.29	24.00
$Cu_2(fsaph)\cdot H_2O$	48.90	2.45	5.32	24.68	48.45	2.59	5.13	23.30
$Cu_2(fsach)\cdot 2H_2O$	46.54	3.72	4.56	21.94	46.40	3.89	4.92	22.32
$Ni_2(fsaen)\cdot 3H_2O$	40.98	3.34	5.26	22.15	41.28	3.46	5.35	22.42
$Ni_2(fsapn)\cdot 3H_2O$	42.48	3.81	5.12	22.08	42.44	3.75	5.21	21.83
$Ni_2(fsatn)\cdot 5H_2O$	39.37	4.01	4.83	20.26	39.77	4.22	4.88	20.32
$Ni_2(fsaph)\cdot 5H_2O$	43.17	3.79	4.45	19.01	43.48	3.65	4.61	19.32
$Ni_2(fsach)\cdot 3H_2O$	45.35	4.33	4.66	20.68	45.72	4.19	4.85	20.32

a) $fsaen^{4-}=C_{18}H_{12}N_2O_6$, $fsapn^{4-}=fsatn^{4-}=C_{19}H_{14}N_2O_6$, $fsaph^{4-}=C_{22}H_{10}N_2O_6$, and $fsach^{4-}=C_{22}H_{18}N_2O_6$.

and to this mixture was added an aqueous solution (15 ml) of copper(II) acetate monohydrate (200 mg). This was heated at 60°C for 30 min and yellowish brown prisms which separated were collected, washed with hot water and dried under reduced pressure.

$Ni_2(fsaen)\cdot 3H_2O$. To a warm aqueous solution (30 ml) of 3-formylsalicylic acid (136 mg), ethylenediamine (30 mg) and sodium carbonate (55 mg), an aqueous solution (15 ml) of nickel(II) acetate tetrahydrate (250 mg) was added. The mixture was maintained at this temperature for 1 h. Red prisms which separated were collected, thoroughly washed with hot water, and dried under reduced pressure.

Elemental analyses of the mononuclear and binuclear metal complexes are given in Table 1.

Measurements. Infrared spectra were measured with a Hitachi 215 grating infrared spectrometer on a KBr disk. Reflectance spectra were recorded with a Shimadzu multipurpose spectrophotometer Model MPS-5000. Magnetic susceptibilities were measured by the Faraday method from liquid nitrogen temperature to room temperature. Diamagnetic correction was done using the Pascal constants.[6] Effective magnetic moment was calculated by the equation, $\mu_{eff}=2.828\sqrt{(\chi_A-N\alpha)T}$. The temperature-independent paramagnetism, $N\alpha$, for a paramagnetic nickel(II) ion is estimated at 193×10^{-6} e.m.u./mol.[7]

Results and Discussion

TABLE 2. COLOR, SPECTRAL DATA, AND MAGNETIC MOMENTS OF MONONUCLEAR COMPLEXES

Complex	Color	Infrared (cm^{-1}) C=O	C=N	Visible (cm^{-1})	μ_{eff} (T(K)) (B.M.)
$Cu(H_2fsaen)\cdot 1/2H_2O$	purple	1705	1645	18100	1.85 (294.3)
$Cu(H_2fsapn)\cdot 1/2H_2O$	purple	1705	1645	18200	1.84 (292.9)
$Ni(H_2fsaen)\cdot 1/2H_2O$	yellow	1725	1635	18500	diamag.
$Ni(H_2fsapn)\cdot 1/2H_2O$	orange	1720	1635	18600	diamag.

Mononuclear Complexes. Color and physical properties for the mononuclear complexes are tabulated in Table 2. The infrared absorption bands at 1725—1705 and at 1645—1635 cm^{-1} are tentatively assigned to the C=O stretching vibration of free carboxyl group and the coordinated azomethin group respectively. The ligand field band for $Cu(H_2fsaen)\cdot 1/2H_2O$ and for $Cu(H_2fsapn)\cdot 1/2H_2O$ well corresponds to the band for *N,N'*-disalicylideneethylenediaminatocopper(II)[8-10] and for *N,N'*-disalicylidenepropylenediaminatocopper(II)[10,11] respectively. The room temperature magnetic moment for $Cu(H_2fsaen)\cdot 1/2H_2O$ and for $Cu(H_2fsapn)\cdot 1/2H_2O$ also is substantially equal to 1.84 B.M.[12] for *N,N'*-disalicylideneethylenediaminatocopper(II) and 1.81 B.M.[12] for *N,N'*-disalicylidenepropylenediaminatocopper(II) respectively. These facts imply that each of the present complexes has a similar structure to the corresponding *N,N'*-disalicylidenealkylenediaminatocopper(II) complex.

It is clear that $Ni(H_2fsaen)\cdot 1/2H_2O$ and $Ni(H_2fsapn)\cdot$

TABLE 3. COLOR, SPECTRAL DATA AND MAGNETIC MOMENTS OF BINUCLEAR COPPER(II) COMPLEXES

Complex	Color	Infrared (cm^{-1}) C=O	C=N	Visible (cm^{-1})		$\mu_{eff}(T(K))$ (B.M.)
$Cu_2(fsaen)\cdot 2H_2O$	yellowish brown	1565	1640	13400	18200	0.76(295.4)
$Cu_2(fsapn)\cdot 2H_2O$	yellowish brown	1560	1630	13000	18000	0.85(299.0)
$Cu_2(fsatn)\cdot 2H_2O$	blue	1580	1630	14600	17500	0.68(295.4)
$Cu_2(fsaph)\cdot H_2O$	brown	1550	1620	15000	18000	0.89(296.7)
$Cu_2(fsach)\cdot 2H_2O$	yellowish brown	1560	1635	15100	17400	1.03(298.4)

$1/2H_2O$ have a planar configuration, since they are diamagnetic and their reflectance spectra possess only one ligand field band around 18500 cm^{-1}, which corresponds to the band for *N,N'*-disalicylideneethylenediaminatonickel(II)[10] and *N,N'*-disalicylidenepropylenediaminatonickel(II).[10]

Binuclear Copper(II) Complexes. In Table 3 color, infrared and visible absorption bands, and effective magnetic moments for the binuclear copper(II) complexes are given. No absorption band was found in the region 1750—1650 cm^{-1}. Instead a broad and strong band was found around 1550—1580 cm^{-1}. In general the $\nu_{C=O}$ mode of carboxyl shifts to lower frequency by coordination.[13] In the case of binuclear complexes of 3-formylsalicylic acid[3] and its Schiff bases,[4] the C=O stretching vibration was found around 1550 cm^{-1}. Therefore it seems reasonable to assign the band at 1580—1550 cm^{-1} to the coordinated carboxylate group.

The reflectance spectra of the complexes show two bands in the visible region. The second (higher energy) band for $Cu_2(fsaen)\cdot 2H_2O$ and for $Cu_2(fsapn)\cdot 2H_2O$ is well in accordance with the band for $Cu(H_2fsaen)\cdot 1/2H_2O$ and for $Cu(H_2fsapn)\cdot 1/2H_2O$, respectively. The position of the second band for $Cu_2(fsaph)\cdot H_2O$ is practically equal to that of the band (17900 cm^{-1}) for *N, N'*-disalicylidene-*o*-phenylenediaminatocopper(II).[10,12] Therefore, the second band was tentatively assigned to the "inside" copper(II) (CuN_2O_2-chromophor). The band at 17500 cm^{-1} for $Cu_2(fsatn)\cdot 2H_2O$ is considerably higher in energy compared with 16600 cm^{-1} [10] for *N,N'*-disalicylidenetrimethylenediaminatocopper(II). Sinn *et al.*[12,14] have found that dichloro[*N,N'*-disalicylidenetrimethylenediaminatocopper(II)]copper(II) and dichloro[*N, N'*-disalicylidenetrimethylenediaminatocopper(II)]zinc(II) have a d-d band at 17100 cm^{-1}. This fact implies that the coplanarity of the $\begin{smallmatrix}N\diagdown & & \diagup O\\ & Cu & \\ N\diagup & & \diagdown O\end{smallmatrix}$ plane in *N,N'*-disalicylidenetrimethylenediaminatocopper(II) is enhanced on forming a binuclear complex bridged by the phenolic oxygen.[12,14] Therefore the band at 17500 cm^{-1} of $Cu_2(fsatn)\cdot 2H_2O$ is attributed to the [CuN_2O_2]-chromophor. On the other hand, the first (lower energy) band is tentatively assigned to the "outside" copper(II) ion. It is not clear if a water molecule coordinates to the "outside" copper from an apical direction.

Sub-normal magnetic moments of the complexes at room temperature suggest a partial spin-pairing between copper(II) ions. The magnetic susceptibility was measured at various temperatures (77.4—300 K). The results are shown in Fig. 3. The magnetisms were well interpreted in terms of the Bleaney-Bowers equation,[15]

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(-2J/kT\right)\right]^{-1} + N\alpha,$$

where J is the exchange integral, k the Boltzmann constant, N the Avogadro number, β the Bohr magneton, and g the Lande g-factor. The magnetic parameters, $-2J$, g, and $N\alpha$, obtained from the best fit of the experimental values to the theoretical values are given in Table 4.

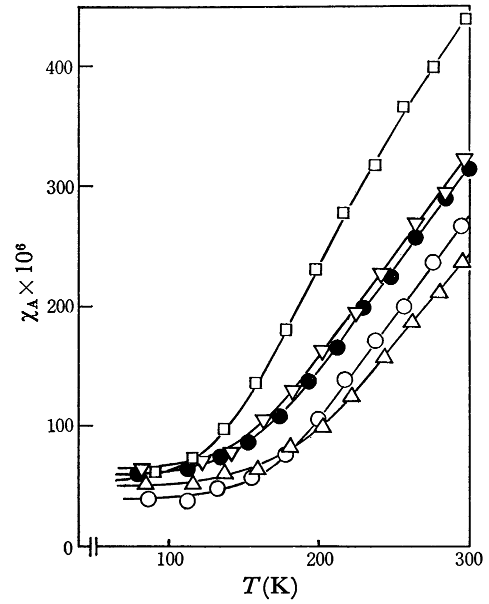


Fig. 3. Temperature variation of magnetic susceptibility of (○)$Cu_2(fsaen)\cdot 2H_2O$, (●)$Cu_2(fsapn)\cdot 2H_2O$, (△) $Cu_2(fsatn)\cdot 2H_2O$, (▽)$Cu_2(fsaph)\cdot H_2O$, and (□)$Cu_2(fsach)\cdot 2H_2O$.

TABLE 4. MAGNETIC PARAMETERS, $-2J$, g, AND $N\alpha$, FOR BINUCLEAR COPPER(II) COMPLEXES

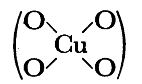
Complex	$-2J$ (cm^{-1})	g	$N\alpha\times 10^6$ (c.g.s./mol)
$Cu_2(fsaen)\cdot 2H_2O$	660	2.20	40
$Cu_2(fsapn)\cdot 2H_2O$	655	2.20	60
$Cu_2(fsatn)\cdot 2H_2O$	720	2.20	50
$Cu_2(fsaph)\cdot H_2O$	650	2.20	65
$Cu_2(fsach)\cdot 2H_2O$	555	2.20	55

It is well known[12,14,16,17] that the copper(II) complexes with the tetradentate Schiff bases of salicylaldehyde form binuclear copper(II) complexes bridged by the phenolic oxygens when treated with copper(II) chloride or copper(II) bromide. The magnetic properties of these complexes have been elucidated by Sinn *et al.*,[16] and the $-2J$ values, the energy separation between the singlet and triplet states, are evaluated at 98—472 cm^{-1}. It is apparent that the present complexes exhibit a stronger antiferromagnetic spin-exchange interaction compared with dihalogeno[*N,N'*-disalicylidenealkylenediaminatocopper(II)]copper(II) complexes. In these complexes it seems that the steric hindrance between the halogen and the hydrogen attached to the 3-position (next to the phenolic oxygen) of the aromatic ring is sufficiently large to deform the $\begin{smallmatrix}O\diagdown & & \diagup X\\ & Cu & \\ O\diagup & & \diagdown X\end{smallmatrix}$ (X=halogen) plane to a pseudotetrahedral geometry.[16,18] In fact it was demonstrated from X-ray analysis[19] that the "outside" configuration of dichloro[*N, N'*-disalicylideneethylenediaminatocopper(II)]copper(II) is pseudotetrahedral. On the other hand, no steric hindrance is expected in our complexes, since the carboxyl group attached to the 3-position of the salicylaldehyde moiety takes part in coordination. Thus

Table 5. Color, spectral data, and magnetic moments of binuclear nickel(II) complexes

Complex	Color	Infrared (cm^{-1})		Visible (cm^{-1})			$\mu_{eff}(T(K))$[a) (B.M.)
		C=O	C=N				
$\mathrm{Ni_2(fsaen)\cdot 3H_2O}$	red	1555	1623	9400	16000	18300	2.17(295.3) [3.14]
$\mathrm{Ni_2(fsapn)\cdot 3H_2O}$	orange	1555	1625	9600	15000	18700	2.27(299.0) [3.23]
$\mathrm{Ni_2(fsatn)\cdot 5H_2O}$	blue	1560	1635	8200 14500	9700 17100	12400	3.36(298.3)
$\mathrm{Ni_2(fsaph)\cdot 5H_2O}$	reddish orange	1550	1620	9500	15500	18500	2.33(296.6) [3.28]
$\mathrm{Ni_2(fsach)\cdot 3H_2O}$	orange	1555	1625	9100	14800	18500	2.25(294.8) [3.21]

a) Magnetic moment per nickel(II) ion. The value in a bracket is calculated on the assumption that one of nickel(II) ions is diamagnetic.

the configuration of the "outside" copper  is substantially planar and two tetragonal planes of the "inside" and "outside" copper(II) ions form a coplane. Thereby the spin exchange between the metal ions may be efficiently caused by a super-exchange mechanism through the oxygen P_π-orbitals.[20)

Binuclear Nickel(II) Complexes. The infrared spectra of the binuclear nickel(II) complexes are similar to those of the corresponding copper(II) complexes. Each reflectance spectrum of $\mathrm{Ni_2(fsaen)\cdot 3H_2O}$, $\mathrm{Ni_2(fsapn)\cdot 3H_2O}$, $\mathrm{Ni_2(fsaph)\cdot 5H_2O}$, and $\mathrm{Ni_2(fsach)\cdot 3H_2O}$ has three d-d bands in visible region. The band around 18500 cm^{-1} seems to correspond to the band for the mononuclear nickel(II) complexes. The bands around 9500 and 15500 cm^{-1} imply that these complexes contain a nickel(II) of octahedral configuration. Accordingly, the coordination of water from apical positions was supposed for the "outside" nickel. The bands around 9500 and 15500 cm^{-1} were assigned to the ${}^3T_{2g}\leftarrow{}^3A_{2g}$ and ${}^3T_{1g}\leftarrow{}^3A_{2g}$ transitions respectively. Since the 10 Dq for hexaaquonickel(II) is estimated at 8500 cm^{-1},[21) the ligand field in the present complexes is stronger than H_2O.

The magnetic moments calculated per one nickel(II) ion are much lower than the spin-only value 2.83 B.M. This may be explained by (a) antiferromagnetic spin-pairing between paramagnetic nickel(II) ions or (b) formation of binuclear complex containing one paramagnetic and one diamagnetic nickel(II) ions. The visible spectra of the complexes seem to support the latter possibility. In order to obtain further evidence magnetic susceptibility was measured at various temperatures. In Fig. 4, $1/(\chi_A - N\alpha)$ is plotted against temperature. As is seen in Fig. 4 the magnetisms of the complexes are well interpreted in terms of the Curie-Weiss law ($\chi_A = C/(T-\theta)$). It should be noted that the Weiss constants are very small (at best 4 K). The phenolic oxygen-briged binuclear nickel(II) complexes so far reported obey the Curie-Weiss law in the range from liquid nitrogen temperature to room temperature with a relatively large Weiss constant more than 30 K.[3,4,22,23) Accordingly it is concluded that $\mathrm{Ni_2(fsaen)\cdot 3H_2O}$, $\mathrm{Ni_2(fsapn)\cdot 3H_2O}$, $\mathrm{Ni_2(fsaph)\cdot 5H_2O}$, and $\mathrm{Ni_2(fsach)\cdot 3H_2O}$ are novel complexes composed of one paramagnetic and one diamagnetic nickel(II) ions. Thus, magnetic moments per binuclear units were calculated to give 3.14—3.28 B.M., which are quite common to a nickel(II) in an octahedral environment.

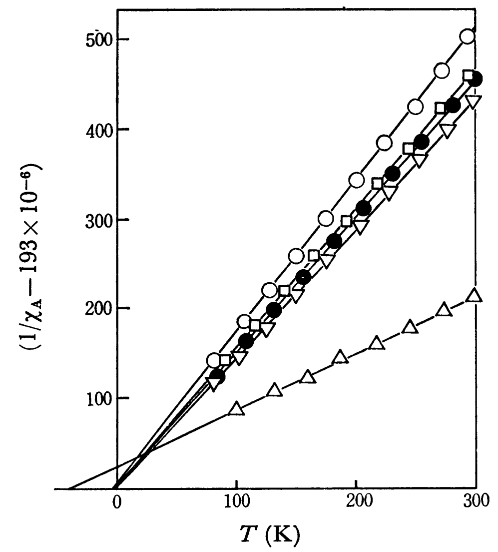


Fig 4. Plots of inverse susceptibilities as a function of temperature for (○)$\mathrm{Ni_2(fsaen)\cdot 3H_2O}$, (●)$\mathrm{Ni_2(fsapn)\cdot 3H_2O}$, (△)$\mathrm{Ni(fsatn)\cdot 5H_2O}$, (▽)$\mathrm{Ni_2(fsaph)\cdot 5H_2O}$, and (□)$\mathrm{Ni_2(fsach)\cdot 3H_2O}$ per a nickel atom.

Paramagnetic-diamagnetic binuclear nickel(II) complexes are rare.[22) The success in synthesizing paramagnetic-diamagnetic binuclear nickel(II) complexes with the present ligands is obviously cocerned with a considerable difference in the ligand field strength between the "inside" and "outside" coordination sites. The coordinatively selective property of the ligands also leads to the formation of the copper(II)-paramagnetic nickel(II) complex (CuNi(fsaen))[24) and other hetero-metal binuclear complexes.[25) The Schiff bases derived from 1,3,5-triketones and diamines,[26—29) which are similar in coordinating mode to our ligands, should form paramagnetic-diamagnetic binuclear nickel(II) complexes.

The color and the visible spectrum of $\mathrm{Ni_2(fsatn)\cdot}$

$5H_2O$ are markedly different from other nickel(II) complexes. It is known that *N*,*N*′-disalicylidenetrimethylenediaminatonickel(II) maintains a planar structure.[10,30] However its d-d band is fairly low in energy, demonstrating a weaker ligand field of the ligand with a 6-6-6 condensed ring system compared with the tetradentate salicylaldehyde-Schiff bases with a 6-5-6 condensed ring system. The binuclear nickel(II) complex of the macrocycle obtained from 2-hydroxy-5-methylisophthalaldehyde and 1,3-propanediamine (nickel(II) ions are bridged by the phenolic oxygens) is known to have a high-spin state, where the nickel is coordinated with chloride ion in the apical position.[23] From this fact it is likely that the "inside" ligand field strength of H_4fsatn decreases to allow the fifth (and the sixth) coordination from an apical position when the phenolic oxygen operates as a bridge. The room temperature magnetic moment of Ni_2(fsatn)·$5H_2O$ is 3.36 B.M. per one nickel(II) ion. The magnetic moment decreases with lowering of temperature to 2.97 B.M. at 87.5 K. The $1/(\chi_A - N\alpha)$ plots against temperature obey the Curie-Weiss law with the large Weiss constant −40 K. This value is quite comparable to those (−35—−41 K) found for the binuclear nickel(II) complexes of 3-formylsalicylic acid–monoamine Schiff bases.[4] Thus it is evident that Ni_2(fsatn)·$5H_2O$ is a binuclear complex composed of two paramagnetic nickel(II) ions.

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