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Magnetic and Spectral Properties of Binuclear Nickel(II) Nitrato and Acetato Complexes of Tridentate Schiff Bases Derived from Salicylaldehydes and *N*-Substituted Trimethylenediamines

Tadashi Tokii, Shuji Emori, and Yoneichiro Muto*

Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840

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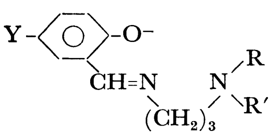
A new series of binuclear Ni(II) complexes with the empirical formula Ni(5-Y-sal·pr·NRR′)X has been prepared by the reaction of the parent complexes, Ni(5-Y-sal·pr·NRR′)$_2$ with metal salts NiX$_2$, where 5-Y-sal·pr·NRR′=Schiff base ligand derived from 5-substituted salicylaldehyde and *N*-substituted trimethylenediamine, R=H or CH$_3$, R′=CH$_3$, Y=H or Cl and X=NO$_3$ or CH$_3$COO. The nature of the complexes has been confirmed to be dimeric on the basis of the results of molecular weight, magnetic and spectral measurements. The values of exchange integral, $J=-10$—-15 cm^{-1}, have been evaluated for the Ni(II) complexes from their temperature dependences of magnetic susceptibilities. The antiferromagnetic property has been discussed in terms of structural considerations. For comparison, the corresponding Cu(II) complexes Cu(5-Y-sal·pr·NRR′)X have been prepared and investigated.

Although a large number of phenolic oxygen-bridged binuclear Cu(II) complexes with *N*-substituted salicylideneaminato ligands have been synthesized and characterized,[1,2] relatively few Ni(II) complexes analogous to the Cu(II) complexes have been prepared, the work of Butcher and Sinn[3] represents an attempt at investigation; the Ni(II) complexes are represented by the formula [Ni(bsb)NO$_3$·C$_2$H$_5$OH]$_2$, where bsb represents a bidentate Schiff base.

In a previous paper,[4] it was reported that bis[*N*-(3-dimethylaminopropyl)salicylideneaminato]copper(II), Cu(Sal·pr·NMe$_2$)$_2$, reacts with copper(II) chloride to yield a binuclear complex with the formula [Cu(Sal·pr·NMe$_2$)Cl]$_2$ in which the phenolic oxygen atoms act as bridges and each of the two organic ligands is tridentately coordinated to a single metal ion. Attempts to prepare the corresponding Ni(II) complex, [Ni(Sal·pr·NMe$_2$)Cl]$_2$, however, were unsuccessful. Six complexes with the stoichiometry of Ni(5-Y-sal·pr·NRR′)X, where X=NO$_3$ or CH$_3$COO and 5-Y-sal·pr·NRR′ represents the tridentate salicylideneaminato ligand of the general formula, have now been isolated



Abbreviation:
Sal·pr·NHMe; R=H, R′=CH$_3$, Y=H
Sal·pr·NMe$_2$; R=R′=CH$_3$, Y=H
5-Cl-sal·pr·NHMe; R=H, R′=CH$_3$, Y=Cl
5-Cl-sal·pr·NMe$_2$; R=R′=CH$_3$, Y=Cl

The dimeric octahedral structure has been established by comparing the IR and electronic reflectance spectra, molecular weights, and magnetic susceptibilities with those of the corresponding Cu(II) complexes, Cu(5-Y-sal·pr·NRR′)X, which have been prepared in the present study and confirmed to be monomeric. It is noteworthy that the Ni(II) complexes exhibit antiferromagnetism in contrast to [Ni(bsb)NO$_3$·C$_2$H$_5$OH]$_2$ which shows intramolecular ferromagnetic interaction.[3]

The results of characterization studies on the newly prepared complexes will be reported and the differences in magnetic properties between Ni(5-Y-sal·pr·NRR′)X and [Ni(bsb)NO$_3$·C$_2$H$_5$OH]$_2$ will be discussed from structural considerations.

Experimental

Syntheses. *Ni(5-Y-sal·pr·NRR′)NO$_3$ Complexes*: A typical synthetic method is as follows. A solution of Ni(NO$_3$)$_2$·6H$_2$O (11 mmol) in ethanol (50 ml) was added to a solution of one of the parent Ni(5-Y-sal·pr·NRR′)$_2$ complexes (10 mmol) in ethanol (100 ml), and the mixture was stirred on a hot plate for 1/2 h. The green crystals thus precipitated were collected, washed repeatedly with ethanol and dried.

Ni(5-Y-sal·pr·NHMe)CH$_3$COO Complexes: A solution of Ni(CH$_3$COO)$_2$·4H$_2$O (11 mmol) in ethanol (50 ml) was added to one of the parent Ni(5-Y-sal·pr·NHMe)$_2$ complexes (10 mmol) suspended in chloroform (50 ml). The solution was stirred at *ca.* 50 °C for 1/2 h and concentrated to one-third of the volume. After the solution had been allowed to stand overnight at *ca.* 5 °C in a freezer, the separated green crystals were collected and washed twice with a small quantity of ethanol and once with ether.

Cu(Sal·pr·NMe$_2$)NO$_3$ Complex: This complex was prepared by the reaction of Cu(Sal·pr·NMe$_2$)$_2$ and Cu(NO$_3$)$_2$·3H$_2$O using the same procedure as for Ni(5-Y-sal·pr·NRR′)NO$_3$ complexes. The purification was made by recrystallization from ethanol.

Cu(5-Y-sal·pr·NHMe)X Complexes: A solution of CuX$_2$·nH$_2$O (11 mmol) in ethanol (50 ml) was added to a mixture of bis(5-substituted salicylaldehydato)copper(II) (10 mmol) and *N*-methyl-1,3-propanediamine (20 mmol) in ethanol (50 ml). The solution was stirred at *ca.* 70 °C for 1/2 h and concentrated to one half of the volume. After the solution had been allowed to stand overnight at *ca.* 5 °C in a freezer, the separated green crystals were collected and recrystallized from ethanol.

The elemental analyses for the new compounds are summarized in Table 1.

Physical Measurements. The molecular weights of the complexes **5**—**9** listed in Table 1 were determined osmometrically with a Hitachi Molecular Weight Apparatus 117, the results of which are given in Table 2. Magnetic susceptibilities of all the complexes **1**—**10** were determined by the Gouy method in the temperature range 80—300 K. For complex **2**, the susceptibilities in the temperature range 4.2—80 K were determined by the Faraday method. Effective magnetic moments were calculated from the equation:

$$\mu_{\text{eff}} = 2.83\sqrt{(\chi_A - N_\alpha)\cdot T} \tag{1}$$

where χ_A is the molar magnetic susceptibility corrected for the diamagnetism of the constituted atoms using Pascal's

TABLE 1. ANALYTICAL DATA

	Complex	Found (%)				Calcd (%)			
		C	H	N	Metal	C	H	N	Metal
1	Ni(Sal·pr·NHMe)NO_3	42.44	4.93	13.35	18.71	42.35	4.85	13.47	18.82
2	Ni(Sal·pr·NMe_2)NO_3	44.14	5.30	12.66	17.84	44.21	5.26	12.89	18.01
3	Ni(5-Cl-sal·pr·NHMe)NO_3	38.61	4.08	11.68	16.88	38.14	4.07	12.13	16.95
4	Ni(5-Cl-sal·pr·NMe_2)NO_3	39.82	4.49	11.44	16.43	39.99	4.48	11.66	16.29
5	Ni(Sal·pr·NHMe)CH_3COO	50.47	5.75	8.86	18.91	50.53	5.87	9.06	19.00
6	Ni(5-Cl-sal·pr·NHMe)CH_3COO	45.06	4.89	7.92	17.09	45.46	4.99	8.16	17.09
7	Cu(sal·pr·NHMe)NO_3	41.80	4.75	13.01	20.09	41.70	4.77	13.26	20.06
8	Cu(Sal·pr·NMe_2)NO_3	43.46	5.16	12.77	19.14	43.57	5.18	12.70	19.21
9	Cu(Sal·pr·NHMe)CH_3COO	49.72	5.80	8.97	20.30	49.75	5.78	8.93	20.25
10	Cu(5-Cl-sal·pr·NHMe)CH_3COO	44.78	4.93	8.07	18.22	44.83	4.92	8.04	18.24

TABLE 2. MOLECULAR WEIGHT DATA

	Complex	Solvent	Concentration (10^{-3} mol·dm^{-3})	Molecular weight	
				Obsd	Calcd
5	Ni(Sal·pr·NHMe)CH_3COO	chloroform	2.86	558	618 (dimer)
6	Ni(5-Cl-sal·pr·NHMe)CH_3COO	chloroform	3.26	632	687 (dimer)
7	Cu(Sal·pr·NHMe)NO_3	acetone	2.86	312	317 (monomer)
8	Cu(Sal·pr·NMe_2)NO_3	acetonitrile	3.44	311	331 (monomer)
9	Cu(Sal·pr·NHMe)CH_3COO	benzene	4.67	354	314 (monomer)

TABLE 3. MAGNETIC DATA

	Complex	μ_{eff}/B.M. (T/K)	C	θ/K	g	J/cm^{-1}
1	Ni(Sal·pr·NHMe)NO_3	2.97(290), 2.59(80)	1.262	−36	2.25	−14
2	Ni(Sal·pr·NMe_2)NO_3	3.10(299), 2.75(80), 0.28(4.2)	1.305	−29	2.28	−9.6[a)]
3	Ni(5-Cl-sal·pr·NHMe)NO_3	3.16(292), 2.72(79)	1.436	−43	2.40	−14
4	Ni(5-Cl-sal·pr·NMe_2)NO_3	3.09(302), 2.68(78)	1.332	−35	2.31	−14
5	Ni(Sal·pr·NHMe)CH_3COO	2.98(293), 2.64(79)	1.229	−29	2.22	−14
6	Ni(5-Cl-sal·pr·NHMe)CH_3COO	3.02(293), 2.58(78)	1.334	−47	2.31	−15
7	Cu(Sal·pr·NHMe)NO_3	1.82(300), 1.82(78)	0.413	0	2.10	
8	Cu(Sal·pr·NMe_2)NO_3	1.82(300), 1.80(78)	0.414	0	2.10	
9	Cu(Sal·pr·NHMe)CH_3COO	1.83(303), 1.80(78)	0.410	0	2.09	
10	Cu(5-Cl-sal·pr·NHMe)CH_3COO	1.83(303), 1.80(78)	0.410	0	2.09	

a) The value was evaluated from the magnetic susceptibility data in the temperature range 4.2−300 K (*cf.* text).

constant[5)] and N_α is the temperature-independent paramagnetism per gram-ion of Ni(II) or Cu(II). The N_α value of 200×10^{-6} and 60×10^{-6} cgs, emu were assumed for Ni(II)[6)] and Cu(II),[7)] respectively, and a set of the results is given in Table 3. The reflectance spectra were recorded with a Hitachi Recording Spectrophotometer 323. IR spectral measurements were made with a Hitachi EPI-G2 IR Spectrophotometer in the 400—4000 cm^{-1} region using Nujol mulls.

Results and Discussion

Molecular Weights. Molecular Weight measurements of the Ni(II) acetato complexes **5** and **6** listed in Table 1 were made osmometrically in chloroform, the results of which are given in Table 2. The molecular weights were found to be twice the empirical formula of Ni(5-Y-sal·pr·NHMe)CH_3COO, indicating the presence of a dimeric structure. The low solubility of the Ni(II) nitrato complexes **1**—**4** in chloroform or any other conventional solvents, however, did not allow an accurate determination of the molecular weights. The molecular weight determination for the Cu(II) complexes **7**—**9** showed the compounds to be monomeric (*cf.* Table 2).

Magnetic Susceptibilities. The magnetic susceptibilities of the complexes **1**—**10** were determined over the temperature range 80—300 K. The susceptibility data for complexes **1** and **3**—**10** are shown in Figs. 1 and 2 as plots of the reciprocal susceptibility corrected for diamagnetic contribution and temperature-independent magnetism, $(\chi_A-N_\alpha)^{-1}$, *vs.* temperature, T. The data for complex **2** in Fig. 3 is shown as a χ_A *vs.* T plot.

In the temperature range 80—300 K, the susceptibilities of the Ni(II) complexes **1**—**6** follow the Curie-Weiss law. The Curie (C) and Weiss constants (θ) have been evaluated from the slopes of $(\chi_A-N_\alpha)^{-1}$ *vs.* T plots, and the g values calculated from the

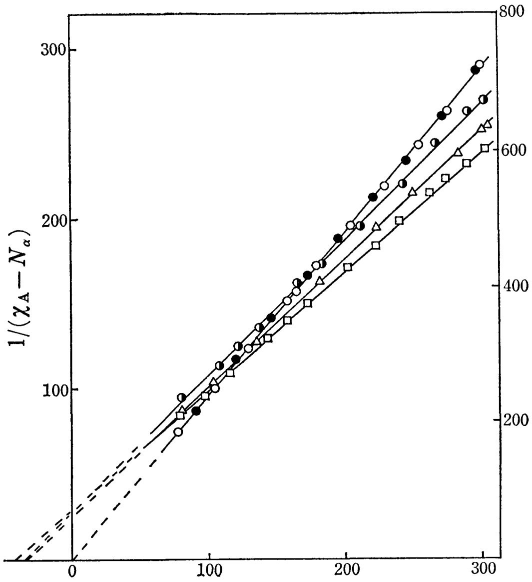


Fig. 1. Variation of magnetic susceptibilities with temperature. Left-hand scale: (◑) Ni(Sal·pr·NHMe)NO$_3$, (□) Ni(5-Cl-sal·pr·NHMe)NO$_3$, (△) Ni(5-Cl-sal·pr·NHMe$_2$)NO$_3$. Right-hand scale: (○) Cu(Sal·pr·NHMe)NO$_3$ (●) Cu(Sal·pr·NMe$_2$)NO$_3$.

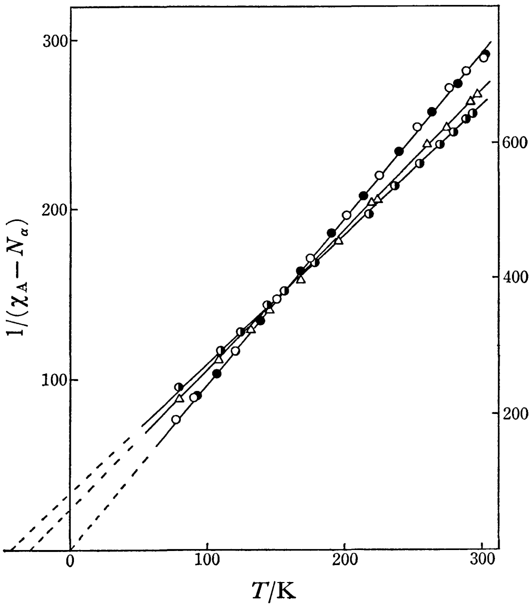


Fig. 2. Variation of magnetic susceptibilities with temperature. Left-hand scale: (△) Ni(Sal·pr·NHMe)CH$_3$COO, (◑) Ni(5-Cl-sal·pr·NHMe)CH$_3$COO. Right-hand scale: (○) Cu(Sal·pr·NHMe)CH$_3$COO, (●) Cu(5-Cl-sal·pr·NHMe)CH$_3$COO.

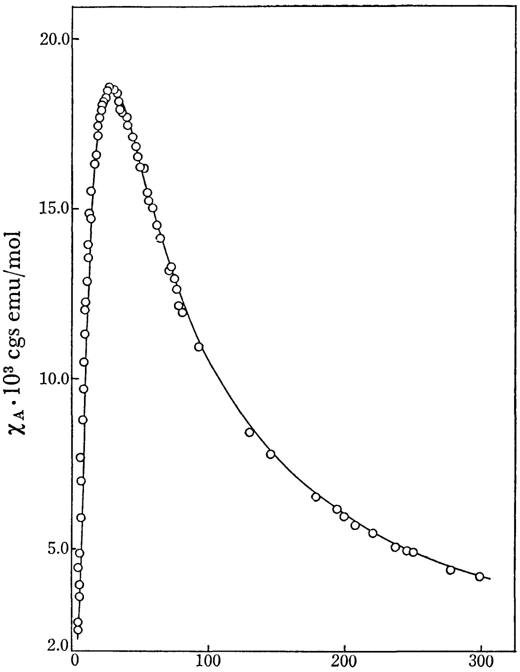


Fig. 3. Observed and calculated magnetic susceptibilities of Ni(Sal·pr·NMe$_2$)NO$_3$: ○, experimental; solid line, calculated by Eq. 2 (*cf.* text).

Curie constants using the relationship $C=N\beta^2g^2[S(S+1)]/3k$ where $S=1$; the results are listed in Table 3. The negative values of the observed Weiss constants (*ca.* −30—−50 K) are indicative of the presence of antiferromagnetic coupling in the Ni(II) complexes. In order to obtain further information about the magnetic interaction, the magnetic susceptibility measurement has been extended for complex **2** from the temperature of liquid nitrogen to that of liquid helium. As can be seen in Fig. 3, the susceptibility χ_A increases with decreasing temperature until a maximum in χ_A is reached at 27 K. At temperatures below 27 K χ_A decreases markedly with decreasing temperature. It has been found that the susceptibility data could be fitted to the susceptibility equation for a Ni(II) dimer:[8]

$$\chi_A = \frac{N\beta^2g^2}{kT}\left[\frac{5+\exp(-4J/kT)}{5+3\exp(-4J/kT)+\exp(-6J/kT)}\right] + N_\alpha \tag{2}$$

where J is exchange integral. The values of $J=-9.6$ cm^{-1} and $g=2.27$ have been evaluated from the best fit of the experimental data to Eq. 2, assuming $N_\alpha=200\times10^{-6}$ cgs emu.[6] The solid line in Fig. 3 represents the susceptibility curve calculated using the parameters. The value of g agrees well with the experimental value of 2.28 determined from the $(\chi_A-N_\alpha)^{-1}$ *vs.* T plot in the temperature range 80—300 K (*cf.* Table 3). The magnetic behavior with a negative J value indicates the presence of antiferromagnetic spin coupling between the Ni(II) ions in the dimeric unit of [Ni(Sal·pr·NMe$_2$)NO$_3$]$_2$. For the other Ni(II) complexes **1** and **3**—**6**, the 80—300 K data gave a good fit to the theoretical curve based on Eq. 2 when the following values were used: the g value evaluated from the $(\chi_A-N_\alpha)^{-1}$ *vs.* T plot, the N_α of 200×10^{-6} cgs emu and the J value listed in Table 3.

The close agreement between the observed and calculated temperature dependences of magnetic susceptibility can be taken as evidence for the presence of a binuclear structure in the Ni(II) complexes.

The susceptibility data of the Cu(II) complexes **7**—**10** follow the Curie law as is seen in Figs. 1 and 2, indicating magnetic dilution in the crystals. Con-

Table 4. Reflectance and IR spectral data

	Complex	Ligand field band maximum, $\tilde{\nu}/10^3$ cm^{-1}	IR absorption, $\tilde{\nu}$/cm^{-1} band maximum[b] near 1540 cm^{-1}	$\tilde{\nu}_{as}CO_2$	$\tilde{\nu}_sCO_2$	Δ_{as-s}
1	Ni(Sal·pr·NHMe)NO_3	16.4, 10.2, 7.8 sh	1550(+16)			
2	Ni(Sal·pr·NMe_2)NO_3	15.7, 9.8, 7.2 sh	1550(+19)			
3	Ni(5-Cl-sal·pr·NHMe)NO_3	16.3, 10.4, 7.9 sh	1538(+24)			
4	Ni(5-Cl-sal·pr·NMe_2)NO_3	15.7, 9.8, 7.1 sh	1537(+17)			
5	Ni(Sal·pr·NHMe)CH_3COO	16.1, 9.9, 7.6 sh	1549(+15)	1566	1447	119
6	Ni(5-Cl-sal·pr·NHMe)CH_3COO	15.9, 9.8, 7.6 sh	1539(+25)	1558	1447	111
7	Cu(Sal·pr·NHMe)NO_3	15.3, 12.5	1541			
8	Cu(Sal·pr·NMe_2)NO_3	15.9, 12.8	1541(+ 7)			
9	Cu(Sal·pr·NHMe)CH_3COO	16.4	1537	1582	1378	204
10	Cu(5-Cl-sal·pr·NHMe)CH_3COO	15.9	1525	1582	1385	197

a) sh=shoulder. b) The numerical values in parentheses indicate the increased wave numbers from the bands in the parent M(5-Y-sal·pr·NRR′)$_2$ complexes where M=Ni(II) or Cu(II).

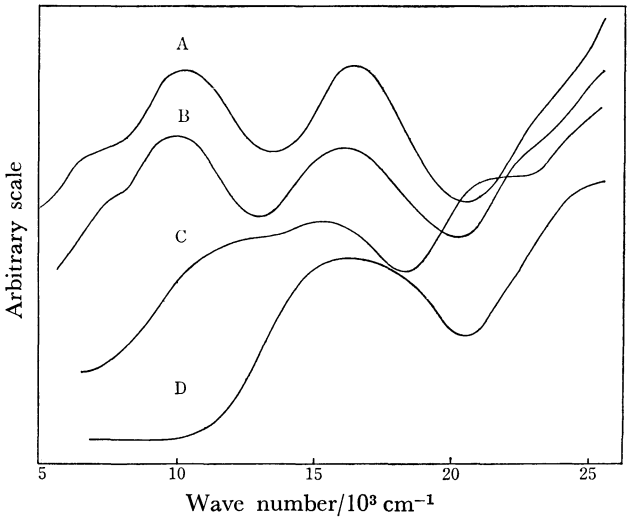


Fig. 4. Reflectance spectra of Ni(Sal·pr·NHMe)NO_3 (A), Ni(Sal·pr·NHMe)CH_3COO (B), Cu(Sal·pr·NHMe)NO_3 (C) and Cu(Sal·pr·NHMe)CH_3COO (D).

sequently in contrast to the Ni(II) complexes, the Cu(II) complexes are considered to be mononuclear.

Diffuse Reflectance Spectra. The present complexes give rise to several bands in the 5000—25000 cm^{-1} region in the diffuse reflectance spectra. The wave numbers of the band maxima are given in Table 4 and the spectral curves for complexes **1**, **5**, **7**, and **9** are shown in Fig. 4.

The Ni(II) complexes investigated all show essentially the same spectral characteristics, two well resolved maxima at *ca.* 16000 and 10000 cm^{-1} with a shoulder at *ca.* 8000 cm^{-1} (*cf.* Table 4 and Fig. 4). This type of spectra is similar to those of the distorted octahedral Ni(II) complexes,[9,10] but quite different from those of the four- or five-coordinated Ni(II) complexes.[11,12] The spectra of the Cu(II) complexes **7** and **8** show a broad band at *ca.* 15500 cm^{-1} with a shoulder at *ca.* 12500 cm^{-1} (*cf.* Table 4 and Fig. 4). This type of spectra is indicative of a five-coordination geometry around the Cu(II) ion and is to be compared with the spectra reported for some distorted square-pyramidal Cu(II) complexes.[4,13,14] The spectral feature of the Cu(II) complexes **9** and **10** is apparently that of a square planar type (*cf.* Fig. 4).

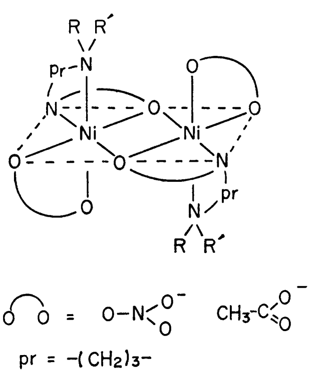
IR Spectra. The wave number of the intense band around 1540 cm^{-1} observed for complexes **1**—**10** are listed in Table 4. For all the Ni(II) complexes studied (**1**—**6**), the absorption energy of the IR band around 1540 cm^{-1} was observed to shift towards higher energies by 15—20 cm^{-1} as compared with that of the corresponding parent bis-complexes Ni(5-Y-sal·pr·NRR′)$_2$, indicating the presence of bridging phenolic oxygen atoms in the nitrato and acetato complexes (*cf.* Table 4).[1—4] No significant band shift was observed for the Cu(II) complex **8**, however, indicating that, in this complex, no phenolic oxygen-bridge exists (*cf.* Table 4). The strong band around 1540 cm^{-1} for each of the Cu(II) complexes **7**,**9**, and **10** also indicates the non-existence of any bridging phenolic oxygen in these complexes.

For the Ni(II) acetato complexes **5** and **6** and the Cu(II) acetato complexes **9** and **10**, the assignment of the IR bands due to the antisymmetric ($\tilde{\nu}_{as}CO_2$) and symmetric ($\tilde{\nu}_sCO_2$) carboxylate stretching vibrations has been made by comparing the bands of the complexes with those of the parent bis-complexes and the corresponding nitrato complexes; the wave numbers are listed in Table 4 together with the separation (Δ_{as-s}) between $\tilde{\nu}_{as}CO_2$ and $\tilde{\nu}_sCO_2$. The correlation between the carboxylate stretching frequencies and structure in Ni(II) acetato complexes has been well established by Curtis.[15] A comparison of the frequencies of $\tilde{\nu}_{as}CO_2$, $\tilde{\nu}_sCO_2$, and Δ_{as-s} for the acetato complexes in this study with those for the Ni(II) acetato complexes of known structure may yield information on the carboxylate coordination in the complexes **5** and **6**. The Ni(II) complexes exhibit $\tilde{\nu}_{as}CO_2$ and $\tilde{\nu}_sCO_2$ bands in an energy region very similar to that reported for the [Ni(tet)CH_3COO]ClO_4·1/2H_2O complex ($\tilde{\nu}_{as}CO_2$ 1550 cm^{-1}, $\tilde{\nu}_sCO_2$ 1448 cm^{-1}, Δ_{as-s} 102 cm^{-1}, tet=*dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane),[15] in which the acetato group is coordinated in a symmetrical chelating mode to the metal ion,[16] and also similar to those reported for the [Ni(en)$_2CH_3COO$] ClO_4 complex ($\tilde{\nu}_{as}CO_2$ 1540 cm^{-1}, $\tilde{\nu}_sCO_2$ 1445 cm^{-1}, Δ_{as-s} 95 cm^{-1})[15] and the $[Ni(1,3\text{-}pr)_2CH_3COO]ClO_4$ complex ($\tilde{\nu}_{as}CO_2$ 1540 cm^{-1}, $\tilde{\nu}_sCO_2$ 1450 cm^{-1}, Δ_{as-s} 90 cm^{-1}),[15] for both of which a symmetrical chelation of the acetato group has been assigned.[15] Thus the close similarity in absorption energy between these complexes leads to the conclusion that the carboxylate coordination mode in the Ni(II) acetato complexes in the present study is of a symmetrical chelating type.

In the case of the Cu(II) acetato complexes **9** and **10**, the $\tilde{\nu}_{as}CO_2$ and $\tilde{\nu}_sCO_2$ bands appear at higher and lower frequencies respectively than those of the ionic acetato ($\tilde{\nu}_{as}CO_2$ 1578 cm^{-1}, $\tilde{\nu}_sCO_2$ 1414 cm^{-1})[17] (*cf.* Table 4), indicating the presence of unidentate coordination of the acetato group in the complexes.[18] The unidentate coordination is consistent with their reflectance spectra showing a four-coordinated planar Cu(II) geometry.

For the nitrato coordination in the Ni(II) nitrato complexes **1**—**4**, no unambiguous assignment could be drawn from the IR spectra, since the 1200—1500 cm^{-1} region was so complicated that no NO stretching bands of the nitrato group could be recognized. The reflectance spectral feature of the complexes is very similar to those of the corresponding acetato complexes indicating a six-coordinated Ni(II) geometry and thus the nitrato coordination mode is considered to be of the symmetrical chelating type. Similarly, the nitrato coordination mode in the Cu(II) nitrato complexes **7** and **8** is presumably a symmetrical chelating type based on the reflectance spectra which show a five-coordinated Cu(II) geometry.

Structure and Magnetic Properties. On the basis of the molecular weight, magnetic and spectral data, the most probable structure for the present Ni(II) complexes **1**—**6** is considered to be I in which the phenolic oxygen atoms act as bridges between the two metal ions and the tridentate ligand 5-Y-sal·pr·NRR′ spans facially due to the long $-(CH_2)_3-$ chain in a manner similar to that in the $Ni(Sal\cdot pr\cdot NMe_2)_2$ complex.[19]



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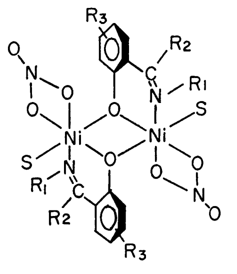

R_1 = Me, CHMe$_2$, Et
R_2 = Ph, H
R_3 = 5-Cl, 5,6-benzo
S = EtOH

II

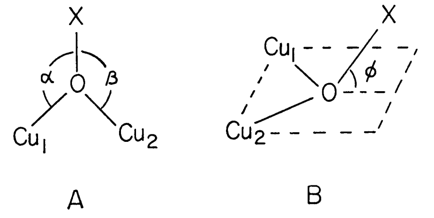

Fig. 5. Geometries around the atom bridging metal ions in phenolic oxygen-bridged binuclear copper(II) complexes.

Structure I should be compared with that of the $[Ni(bsb)NO_3\cdot C_2H_5OH]_2$ complexes which display intramolecular ferromagnetic interaction,[3] the structure of which is shown schematically in II.[3] The most significant difference in structure between I and II is the bonding mode around the bridging phenolic oxygen atoms. As is seen from I and II, the phenolic C–O bonds in the former are coplanar with the plane of the four membered Ni_2O_2 ring due to the chelation of the 5-Y-sal·pr· NRR′ ligand with the phenolic oxygen and azomethine nitrogen atoms at the base of a distorted octahedron, whereas the C–O bonds in the latter are approximately perpendicular to the Ni_2O_2 plane, since the phenolic oxygen atom of the bsb ligand occupies one corner of the basal plane and thus the azomethine nitrogen atom takes one of the axial positions.

In previous papers,[20,21] it was reported that, in binuclear Cu(II) complexes with tridentate salicylaldehyde Schiff bases, the geometry around the atom bridging metal ions is one of the most important factors determining the strength and sign of the magnetic interaction. The structural factors which promote the antiferromagnetic interaction in the complexes are those such as the equality of the angles α and β in Fig. 5A, and the size of the angle ϕ in Fig. 5B (*i.e.*, coplanarity of the O–X bonds with the Cu_1OCu_2O coordination plane, where X is the atom linked to the bridging O atom). These factors may bring about an increase in overlap of the non-orthogonal orbitals involved in the exchange pathways. Recently, Lintvedt *et al.*[22] noted the importance of the planarity of the bridging atom in binuclear Cu(II) complexes for magnetic interaction, and Curtis *et al.*[23] reported that the weak magnetic interaction in di-μ-[4,6,6-trimethyl-3,7-diazanon-3-ene-1,9-diolato(1−)-ONN′, μ-O′]-dicopper(II) diperchlorate ($\theta \approx -25$ K) can be attributed to the nonplanarity of the bridging atom.

From the above structural considerations, the difference in magnetic properties between $[Ni(5\text{-}Y\text{-}sal\cdot pr\cdot NRR')X]_2$ and $[Ni(bsb)NO_3\cdot C_2H_5OH]_2$ is attributable to the different bonding mode of the phenolic C–O bond in the complexes, although, as is the case of $[Ni_2(en)_4Cl_2]Cl_2$,[6] the possibility of the 90° cation-anion-cation type ferromagnetic superexchange interaction as discussed by Kanamori[24] and Goodenough[25] is not excluded since the Ni–O–Ni angle has not been reported in Ref. 3.

For the Cu(II) complexes in the present study, a monomeric five-coordinated structure can be assigned for the nitrato complexes **7** and **8**, and a monomeric square planar structure for the acetato complexes **9** and **10** on the basis of the molecular weight, magnetic, and spectral data. The weaker tendency of Cu(II) to form a six-coordinated complex, as compared with Ni(II), is probably the main factor for the metal to produce the monomeric species.

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