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Spectral and Magnetic Studies on Bi- and Tri-Nuclear Complexes Derived from Copper(II) Complexes with Tetradentate Schiff Base and One of the Chlorides, Nitrates and Perchlorates of Copper(II), Nickel(II), Cobalt(II) and Zinc(II)*[1]

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We have prepared a variety of binuclear and trinuclear complexes of the composition Cu(TDSB)·MX_2 and 2Cu(TDSB)·$M(ClO_4)_2$, where Cu(TDSB)=*N,N'*-ethylenebis(salicylideneiminato)copper(II) or *N,N'*-1,2-propylenebis(salicylideneiminato)copper(II), and M=Co, Ni, Cu and Zn. A few higher polynuclear species were also prepared. The previously reported empirical rule found in binuclear copper(II) complexes, where the two copper ions are in the same environment, that the "higher energies of *d-d* bands - lower magnetic moments," was proved to hold in the binuclear copper complexes of the present study, even though the two copper ions are in different environments. For a series of complexes with M = Cu or other metals, and with X = NO_3 or ClO_4, it was observed that "*d-d* bands of Cu(TDSB) apperas at the shortest wavelengths when M = Cu." For perchlorate complexes, the energy of the *d-d* band is in the order, Co<Ni<Cu>Zn, the same as the Irving and Williams' order of complex stability. It can then be generalized that in a hetero-polynuclear complex molecule, the strengthening of the coordinate bonds around one metal ion strengthens the coordinate bonds around the other metal ion or ions.

Previously we reported the correlation between the magnetism and spectra in binuclear copper(II) halide complexes with pyridine *N*-oxides or salicylideneimines.[1-4] As an extension of these investigations we have been studying a variety of polynuclear complexes derived from copper(II) chelates with tetradentate salicylaldimine-Schiff's base and one of the following metal salts: Cu(II), Ni(II), Co(II) and Zn(II) as the chloride, nitrate, and perchlorate. About the time of the completion of this study, Gruber reported magnetic and spectral studies of similar polynuclear complexes.[5-8]

We are therefore reporting in this paper only the data of the complexes which were not included in their papers except those which are necessary for our discussion. Many of Gruber's and our complexes are adducts with different solvent molecules. Often, too, the numerical values of the data differ in details from each other. The spectral data necessary for the discussion of the stereochemistry are shown in the attached figures.

The present study was initiated to investigate the change in magnetic interaction or spectral properties of binuclear copper(II) complexes when the two copper ions were present in different environments. The rule, "higher energies of *d-d* band-lower magnetic moments," previously observed for the homo-binuclear copper(II) complexes, was to be tested for hetero-binuclear copper(II)

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*[1] A part of this study was presented a) by M. Kato, Y. Muto, H. N. Ramaswamy, H. B. Jonassen, K. Imai and the late K. Ito at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1966, Preprints, Vol. II, p. 135; b) by M. Kato, Y. Muto, H. N. Ramaswamy, H. B. Jonassen and K. Imai at the 16th Conference on Coordination Chemistry of the Chemical Society of Japan, Tokyo (November, 1966), Proceedings, p. 68.

1) M. Kato, Y. Muto and H. B. Jonassen, This Bulletin, **40**, 1738 (1967).

2) Y. Muto, M. Kato, H. B. Jonassen, H. N. Ramaswamy and K. Imai, Proceedings of 10th International Conference on Coordination Chemistry, Nikko, September, 1967, p. 337.

3) Y. Muto, M. Kato, H. B. Jonassen and L. C. Cusachs, This Bulletin, **42**, 417 (1969).

4) M. Kato, Y. Muto, H. B. Jonassen, K. Imai, K. Katsuki and S. Ikegami, *ibid.*, **42**, 2555 (1969).

5) S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Nucl. Chem. Lett.*, **3**, 495 (1967).

6) S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Chem.*, **7**, 268 (1968).

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8) S. J. Gruber, C. M. Harris and E. Sinn, *J. Chem. Phys.*, **49**, 2183 (1968).

TABLE 1. LIST OF THE COMPLEXES BY GRUBER AND CO-WORKERS AND THE PRESENT AUTHORS[†1],[†2],[†3]

Main part of complexes	Solvent molecules attached to the main part of complexes	
	Gruber's	Present study
Cu(En-Sal)		non-adduct (dark green)
Cu(En-Sal)$\cdot$$CuCl_2$	non-adduct	$0.5CH_3OH$ (dark purple)
	H_2O	$0.5C_2H_5OH$ (light purple)
Cu(En-Sal)$\cdot$$Cu(NO_3)_2$	X	non-adduct (purple)
	X	$1.5CH_3OH$ (purple)
	X	$1.5CH_3OH\cdot H_2O$ (brownish purple)
	X	4py (smoked olive)
Cu(En-Sal)$\cdot$$Ni(NO_3)_2$	X	$2C_2H_5OH$ (purple)
Cu(En-Sal)$\cdot$$Co(NO_3)_2$	X	$1.5C_2H_5OH\cdot 0.5H_2O$ (purple)
4Cu(En-Sal)$\cdot$$3Zn(NO_3)_2$	X	non-adduct (brick-red)
Cu(En-Sal)$\cdot$$CoCl_2$	non-adduct	$0.5C_2H_5OH$ (greyish violet)
Cu(En-Sal)$\cdot$$ZnCl_2$	non-adduct	non-adduct (yellowish pink)
2Cu(En-Sal)$\cdot$$Cu(ClO_4)_2$	$3H_2O$	$CH_3OH\cdot 2H_2O$ (dark violet)
2Cu(En-Sal)$\cdot$$Ni(ClO_4)_2$	$3H_2O$	$2H_2O$ (salmon-pink)
2Cu(En-Sal)$\cdot$$Co(ClO_4)_2$	$2.5H_2O$	$2H_2O$ (pink)
2Cu(En-Sal)$\cdot$$Zn(ClO_4)_2$	$1.5H_2O$	$2.5H_2O$ (salmon-pink)
Cu(Pn-Sal)		non-adduct (greyish violet)
Cu(Pn-Sal)$\cdot$$CuCl_2$	non-adduct	non-adduct (dark violet)
Cu(Pn-Sal)$\cdot$$Cu(NO_3)_2$	X	non-adduct (purple)
Cu(Pn-Sal)$\cdot$$Ni(NO_3)_2$	X	$2C_2H_5OH$ (purple)
Cu(Pn-Sal)$\cdot$$Co(NO_3)_2$	X	$1.75C_2H_5OH\cdot 0.5H_2O$ (purple)
Cu(Pn-Sal)$\cdot$$Zn(NO_3)_2$	X	non-adduct (salmon-pink)
2Cu(Pn-Sal)$\cdot$$Zn(NO_3)_2$	X	$1.5CH_3OH\cdot 2H_2O$ (greyish purple)
Cu(Pn-Sal)$\cdot$$CoCl_2$	X	$0.5H_2O$ (greyish violet)
Cu(Pn-Sal)$\cdot$$ZnCl_2$	non-adduct	non-adduct (salmon-pink)
2Cu(Pn-Sal)$\cdot$$Cu(ClO_4)_2$	$2H_2O$	$2H_2O$ (dark violet)
2Cu(Pn-Sal)$\cdot$$Cu(ClO_4)_2$	X	en (greyish green)
Cu(En-AcAc)		non-adduct (dark violet)
2Cu(En-AcAc)$\cdot$$Cu(NO_3)_2$	X	H_2O (greyish brown)

[†1] The symbol(X) in column of Gruber's indicates the complexes which are reported in the present study but not described by Gruber and co-workers.

[†2] Cu(En-Sal), Cu(Pn-Sal) and Cu(En-AcAc) are used as abbreviations for *N,N'*-ethylenebis (salicylideneiminato)copper(II), *N,N'*-1,2-propylenebis (salicylideneiminato) copper (II) and *N,N'*-ethylenebis (acetylacetoneaminato) copper (II) respectively.
en=ethylenediamine, py=pyridine

[†3] Color of the complexes was given in parentheses in the third column.

complexes.*2 The mutual stereochemical interaction between local metal complexes which may occur when more than two metal atoms were present in a molecule, was another interesting point under examination.

The complexes of this study is given in Table 1; some of Gruber's complexes are also included to indicate the difference in the solvation.

Experimental

I. Preparation of Complexes. *A. Materials.* Salicylaldehyde, ethylenediamine, 1,2-propylenediamine (Tokyo Kasei Kogyo's Guaranteed Reagent), metal nitrates, chlorides (Wako Pure Chemical Industries' JIS Special Grade), anhydrous cupric chloride (Fisher Certified Reagent) and perchlorates (K & K Laboratories) were obtained commercially.

B. General Method of Preparation. In a typical preparation, an ethanolic solution of a metal salt was added through a quantitative filter paper to one of the recrystallized parent copper(II) complexes, Cu(En-Sal), Cu(Pn-Sal) or Cu(En-AcAc) in a flask equipped with a condenser. For binuclear complexes, the mole ratio of a chloride or a nitrate to parent complex was 1.1 : 1, *i. e.*, ten per cent excess of the metal salt over the stoichiometric quantity. For the preparation of trinuclear complexes, the mole ratio of the perchlorate or nitrate to the parent complex was 1.1 : 2. The ethanolic mixture in the flask was stirred on a hot plate for two hours to complete the reaction. The product was

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*2 In this paper, the words, hetero- and homo-, are used to indicate the ligand field environments in a polynuclear complex molecule which are essentially different and the same respectively.

filtered off on a glass filter, washed several times with ethanol and once with ether, and dried at 40—50°C.

C. Preparation of Specific Complexes. a) Cu(En-Sal)·$Cu(NO_3)_2$. A crude product was prepared by stirring a mixture of Cu(En-Sal) and $Cu(NO_3)_2 \cdot 3H_2O$ in a 1 : 1 mole ratio in ethanol at room or at an elevated temperature. The product was filtered off, washed with a mixture of ether and ethanol, and dried at 50°C. The pure compound can be prepared by refluxing a recrystallized Cu(En-Sal)·$Cu(NO_3)_2 \cdot 1.5CH_3OH$ in ethanol.

b) Cu(En-Sal)·$Cu(NO_3)_2 \cdot 1.5CH_3OH$. Crude Cu-(En-Sal)·$Cu(NO_3)_2$(5 g) was dissolved by heating in 150 ml of methanol containing one gram of $Cu(NO_3)_2 \cdot 3H_2O$. The hot solution was filtered through a quantitative filter paper into a flask. To the filtrate were slowly added 30 ml of ether and then 120 ml of petroleum ether. The precipitated complex was filtered off, washed with ether containing a small amount of methanol and then with a large amount of ether, and dried at 40—45°C. Yield 2.4 g.

c) Cu(En-Sal)·$Cu(NO_3)_2 \cdot 1.5CH_3OH \cdot H_2O$. Crude Cu(En-Sal)·$Cu(NO_3)_2$(5 g), dissolved in 190 ml methanol on a hot plate and the hot solution was passed once through a quantitative filter paper. To the filtrate, 15 ml of ether and then 130 ml of petroleum ether were slowly added. The product was collected on a glass filter, methanol and ether were added with stirring, and then sucked off. After washing with ether it was dried at 40—45°C, yield 2.9 g.

d) Cu(En-Sal)·$Cu(NO_3)_2 \cdot 4Py$. Three grams of Cu(En-Sal)·$Cu(NO_3)_2$, dissolved in 190 ml of pyridine on a hot plate were filtered through a quantitative filter paper into a flask. Petroleum ether was added until precipitation just occurred. The mixture was allowed to stand for one to two weeks at room temperature with occasional shaking. The product was washed with ether several times, and dried at 50°C,

TABLE 2. ANALYTICAL DATA OF COMPLEXES

Complexes	C%		H%		N%		Metal %	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
Cu(En-Sal)							19.20	19.26
Cu(En-Sal)·$CuCl_2 \cdot 0.5CH_3OH$	41.50	41.26	3.46	3.36	5.98	5.83	26.40	26.46
Cu(En-Sal)·$CuCl_2 \cdot 0.5C_2H_5OH$	42.40	41.90	3.47	3.52	6.09	5.75	26.13	26.08
Cu(En-Sal)·$Cu(NO_3)_2$	37.42	37.14	2.89	2.73	10.59	10.83	24.34	24.56
Cu(En-Sal)·$Cu(NO_3)_2 \cdot 1.5CH_3OH$	36.82	37.17	3.01	3.57	11.25	9.91	22.32	22.47
Cu(En-Sal)·$Cu(NO_3)_2 \cdot 1.5CH_3OH \cdot H_2O$	36.02	36.03	3.70	3.80	10.48	9.60	21.84	21.78
Cu(En-Sal)·$Cu(NO_3)_2 \cdot 4py$	52.05	51.86	4.18	4.11	12.99	13.44	15.31	15.24
Cu(En-Sal)·$Ni(NO_3)_2 \cdot 2C_2H_5OH$	39.89	39.73	4.25	4.33	9.19	9.27	20.60	20.21
Cu(En-Sal)·$Co(NO_3)_2 \cdot 1.5C_2H_5OH \cdot 0.5H_2O$	38.79	38.62	3.78	4.09	9.57	9.48	20.38	20.73
4Cu(En-Sal)·$3Zn(NO_3)_2$	40.25	40.73	2.87	2.99	10.38	10.39	23.87	23.86
Cu(En-Sal)·$CoCl_2 \cdot 0.5C_2H_5OH$	42.48	42.30	3.24	3.55	5.97	5.80	25.71	25.37
Cu(En-Sal)·$ZnCl_2$	41.06	41.23	3.01	3.03	5.98	6.01	27.51	27.66
2Cu(En-Sal)·$Cu(ClO_4)_2 \cdot CH_3OH \cdot 2H_2O$	40.71	40.03	3.94	3.66	5.63	5.66	19.40	19.26
2Cu(En-Sal)·$Ni(ClO_4)_2 \cdot 2H_2O$	40.70	40.31	3.55	3.38	5.51	5.88	19.43	19.49
2Cu(En-Sal)·$Co(ClO_4)_2 \cdot 2H_2O$	40.55	40.31	3.52	3.38	5.60	5.88	19.43	19.51
2Cu(En-Sal)·$Zn(ClO_4)_2 \cdot 2.5H_2O$	40.12	39.66	3.41	3.43	5.84	5.78	20.03	19.86
Cu(Pn-Sal)							18.49	18.48
Cu(Pn-Sal)·$CuCl_2$	42.68	42.69	3.78	3.37	5.97	5.86	26.60	26.57
Cu(Pn-Sal)·$Cu(NO_3)_2$	38.54	38.42	3.26	3.03	10.44	10.54	23.74	23.91
Cu(Pn-Sal)·$Ni(NO_3)_2 \cdot 2C_2H_5OH$	40.64	40.77	4.62	4.56	8.95	9.06	19.67	19.76
Cu(Pn-Sal)·$Co(NO_3)_2$ $1.75C_2H_5OH \cdot 0.5H_2O$	39.84	39.94	4.23	4.50	9.35	9.09	19.73	19.87
Cu(Pn-Sal)·$Zn(NO_3)_2$	38.11	38.29	3.00	3.02	10.45	10.51	24.04	24.18
2Cu(Pn-Sal)·$Zn(NO_3)_2 \cdot 1.5CH_3OH \cdot 2H_2O$	44.41	44.36	4.31	4.40	8.78	8.74	20.12	20.02
Cu(Pn-Sal)·$CoCl_2 \cdot 0.5H_2O$	42.56	42.30	3.52	3.55	5.80	5.80	25.39	25.37
Cu(Pn-Sal)·$ZnCl_2$	42.25	42.53	3.40	3.36	5.66	5.83	26.89	26.85
2Cu(Pn-Sal)·$Cu(ClO_4)_2 \cdot 2H_2O$	41.89	41.41	3.92	3.68	5.55	5.68	19.39	19.33
2Cu(Pn-Sal)·$Cu(ClO_4)_2$·en	42.90	42.80	4.14	3.99	8.23	8.32	19.01	18.87
Cu(En-AcAc)							22.11	22.23
2Cu(En-AcAc)·$Cu(NO_3)_2 \cdot H_2O$	37.13	37.09	5.09	4.93	10.76	10.81	24.52	24.53

yield 1.9 g.

e) $2Cu(Pn\text{-}Sal)\cdot Cu(ClO_4)_2\cdot en$. To a mixture of recrystallized $Cu(en)_2(ClO_4)_2$(2.8 g) and Cu(Pn-Sal) (5.2 g) in a flask, was added a solution of $Cu(ClO_4)_2\cdot 6H_2O$ (3 g) in methanol (130 m*l*). The methanolic mixture was stirred on a hot plate under reflux for three hours. The reaction product was carefully poured into another flask in order to separate it from the small amount of unreacted $Cu(en)_2(ClO_4)_2$. To this, was added 0.2 g of pure $Cu(Pn\text{-}Sal)\cdot Cu(ClO_4)_2\cdot 2H_2O$ and, with stirring, refluxed for five hours more. The dark green fine crystals were washed on a glass filter several times with methanol and once with ether and dried at 80°C, yield 6 g.

f) $2Cu(Pn\text{-}Sal)\cdot Zn(NO_3)_2\cdot 1.5CH_3OH\cdot 2H_2O$. Cu-(Pn-Sal) (2.5 g) and $Zn(NO_3)_2\cdot 6H_2O$ (2.5 g), dissolved in methanol (25 m*l*) by heating gently, was filtered into a flask and allowed to stand until precipitation started. Ether was added to the supernatant to complete the precipitation. The crude material (3.2 g), after dissolving by warming in methanol (20 m*l*), and filtering through a quantitative filter paper into a flask, was placed in a vacuum desiccator. The filtrate was concentrated to one third of its original volume by warming gently under gentle suction. Ether was added to it and the precipitated violet powder was washed on a glass filter with a mixture of ether and methanol several times and once with ether, and dried at 40°C. Yield 2.5 g.

g) $Cu(Pn\text{-}Sal)\cdot Zn(NO_3)_2$. The crude material was prepared by treating a mixture of Cu(Pn-Sal) (3 g) and $Zn(NO_3)_2\cdot 6H_2O$ (3 g) in 30 m*l* of ethanol according to the method of (f). Yield 3.8 g. This was dissolved in methanol (30 m*l*) and filtered through a quantitative filter paper into a flask. By alternatively adding small portions of ether and petroleum ether in volume ratio of 2 : 1 at a time precipitation occurred. The precipitate was filtered, washed with a mixture of ether and methanol twice and once with ether, dried at 95°C, yield 2.7 g.

h) $2Cu(En\text{-}AcAc)\cdot Cu(NO_3)_2\cdot H_2O$. A mixture of Cu(En-AcAc) and $Cu(NO_3)_2\cdot 3H_2O$ in mole ratio of 2 : 1 was dissolved in methanol. The brown solution was concentrated to a certain volume in an evaporator and ether was added to it. The crude product (2.7 g) was dissolved in hot methanol (13 m*l*), filtered through a quantitative filter paper into a flask, and concentrated in an evaporator until precipitation began to occur. After slowly adding 20 m*l* of ether to it, the product was washed with a mixture of ether and methanol several times and once with ether, and dried at 40°C, yield 2 g.

The analytical data for all the complexes are listed in Table 2.

II. Magnetic Susceptibility Determinations. These data were obtained by the Gouy method at room temperature. The molar susceptibility, χ_M, was corrected using Pascal's constants, for the diamagnetism

TABLE 3. MAGNETIC DATA OF COMPLEXES

Complexes	Susceptibility $\chi_g\cdot 10^6$ (cgs, emu)	Temperature (°K)	μ_{eff} (B.M.)	$\mu_{eff}^{25°C}$ (B.M.)
Cu(En-Sal)	3.77	292	1.81	
$Cu(En\text{-}Sal)\cdot CuCl_2\cdot 0.5CH_3OH$	3.67	290	1.52	1.54
$Cu(En\text{-}Sal)\cdot CuCl_2\cdot 0.5C_2H_5OH$	3.74	289	1.55	1.56
$Cu(En\text{-}Sal)\cdot Cu(NO_3)_2$	2.06	304	1.25	1.23
$Cu(En\text{-}Sal)\cdot Cu(NO_3)_2\cdot 1.5CH_3OH$	2.69	301	1.46	1.45
$Cu(En\text{-}Sal)\cdot Cu(NO_3)_2\cdot 1.5CH_3OH\cdot H_2O$	4.06	300	1.76	
$Cu(En\text{-}Sal)\cdot Cu(NO_3)_2\cdot 4py$	2.99	301	1.87	
$Cu(En\text{-}Sal)\cdot Ni(NO_3)_2\cdot 2C_2H_5OH$	8.28	304	3.59	
$Cu(En\text{-}Sal)\cdot Co(NO_3)_2\cdot 1.5C_2H_5OH\cdot 0.5H_2O$	16.26	285	4.75	
$4Cu(En\text{-}Sal)\cdot 3Zn(NO_3)_2$	2.67	284	1.82	
$Cu(En\text{-}Sal)\cdot CoCl_2\cdot 0.5C_2H_5OH$	22.11	284	4.98	
$Cu(En\text{-}Sal)\cdot ZnCl_2$	2.60	284	1.81	
$2Cu(En\text{-}Sal)\cdot Cu(ClO_4)_2\cdot CH_3OH\cdot 2H_2O$	2.17	303	1.45	
$2Cu(En\text{-}Sal)\cdot Ni(ClO_4)_2\cdot 2H_2O$	6.15	299	3.88	
$2Cu(En\text{-}Sal)\cdot Co(ClO_4)_2\cdot 2H_2O$	12.72	298	5.48	
$2Cu(En\text{-}Sal)\cdot Zn(ClO_4)_2\cdot 2.5H_2O$	2.50	297	1.84	
Cu(Pn-Sal)	3.81	284	1.84	
$Cu(Pn\text{-}Sal)\cdot CuCl_2$	3.66	300.5	1.55	1.54
$Cu(Pn\text{-}Sal)\cdot Cu(NO_3)_2$	2.40	304	1.35	1.34
$Cu(Pn\text{-}Sal)\cdot Ni(NO_3)_2\cdot 2C_2H_5OH$	7.87	293	3.48	
$Cu(Pn\text{-}Sal)\cdot Co(NO_3)_2\cdot 1.75C_2H_5OH\cdot 0.5H_2O$	15.79	293	4.85	
$Cu(Pn\text{-}Sal)\cdot Zn(NO_3)_2$	2.08	295	1.77	
$2Cu(Pn\text{-}Sal)\cdot Zn(NO_3)_2\cdot 1.5CH_3OH\cdot 2H_2O$	2.48_5	295	1.83	
$Cu(Pn\text{-}Sal)\cdot CoCl_2\cdot 0.5H_2O$	21.39	293	4.98	
$Cu(Pn\text{-}Sal)\cdot ZnCl_2$	2.36	294	1.79	
$2Cu(Pn\text{-}Sal)\cdot Cu(ClO_4)_2\cdot 2H_2O$	1.83	303	1.35	
$2Cu(Pn\text{-}Sal)\cdot Cu(ClO_4)_2\cdot en$	2.21	302	1.48	
$2Cu(En\text{-}AcAc)\cdot Cu(NO_3)_2\cdot H_2O$	4.80_6	286	1.76	

TABLE 4. DATA OF DIFFUSE REFLECTANCE SPECTRA OF COMPLEXES*)

Complexes	Band maxima, $\lambda_{\rm max}$, mμ
$\mathrm{Cu(En\text{-}Sal)}$	395vs,sh 588s,br* 1705vw
$\mathrm{Cu(En\text{-}Sal)\cdot CuCl_2\cdot 0.5CH_3OH}$	375vs,sh 536s,br* 985s,br* 1950vw
$\mathrm{Cu(En\text{-}Sal)\cdot CuCl_2\cdot 0.5C_2H_5OH}$	375vs,sh 536s,br* 990s,br* 1950vw
$\mathrm{Cu(En\text{-}Sal)\cdot Cu(NO_3)_2}$	516s,br* (860 1020)* m,br,dp 1680vw
$\mathrm{Cu(En\text{-}Sal)\cdot Cu(NO_3)_2\cdot 1.5CH_3OH}$	514s* (855 1015)*m,br,dp 1660vw 1970vw
$\mathrm{Cu(En\text{-}Sal)\cdot Cu(NO_3)_2\cdot 1.5CH_3OH\cdot H_2O}$	375vs,sh (515s 750m 960m,br)* 1700vw
$\mathrm{Cu(En\text{-}Sal)\cdot Cu(NO_3)_2\cdot 4py}$	390vs,sh 585s,br* 1005m,br* 1680vw
$\mathrm{Cu(En\text{-}Sal)\cdot Ni(NO_3)_2\cdot 2C_2H_5OH}$	355vs,sh 539s* 735m,sh† 1210m,br† 1700vw 1980vw
$\mathrm{Cu(En\text{-}Sal)\cdot Co(NO_3)_2\cdot 1.5C_2H_5OH\cdot 0.5H_2O}$	385vs,sh (536* 580sh)s, dp 1255m,br† 1690vw 1975vw
$\mathrm{4Cu(En\text{-}Sal)\cdot 3Zn(NO_3)_2}$	385vs,sh 528s,br* 1695vw
$\mathrm{Cu(En\text{-}Sal)\cdot CoCl_2\cdot 0.5C_2H_5OH}$	565vs† (640sh 662)† vs,dp (1370m,sh 1520s)† br,dp 1975s,br
$\mathrm{Cu(En\text{-}Sal)\cdot ZnCl_2}$	(516* 570sh)s,dp 700vw,sh 1695vw
$\mathrm{2Cu(En\text{-}Sal)\cdot Cu(ClO_4)_2\cdot CH_3OH\cdot 2H_2O}$	505vs,br* (980 1110)*s,br,dp 1950vw
$\mathrm{2Cu(En\text{-}Sal)\cdot Ni(ClO_4)_2\cdot 2H_2O}$	350vs,sh 524s* (705sh 785)†w,dp 1310w,br† 1690w 18985vw
$\mathrm{2Cu(En\text{-}Sal)\cdot Co(ClO_4)_2\cdot 2H_2O}$	360vs,sh 527s* 680vw,br,sh 1100w,sh 1415w,br† 1690vw 1985vw
$\mathrm{2Cu(En\text{-}Sal)\cdot Zn(ClO_4)_2\cdot 2.5H_2O}$	355vs,sh 526s* 1690vw 1990vw
$\mathrm{Cu(Pn\text{-}Sal)}$	385vs,br,sh 566s* 1695vw
$\mathrm{Cu(Pn\text{-}Sal)\cdot CuCl_2}$	355vs,sh 515s,br* 945s,br* 1680vw
$\mathrm{Cu(Pn\text{-}Sal)\cdot Cu(NO_3)_2}$	360vs,sh 506s,br* (910 1030)* m,br,dp
$\mathrm{Cu(Pn\text{-}Sal)\cdot Ni(NO_3)_2\cdot 2C_2H_5OH}$	540* (675 750)† m,sh,dp 1205m,br† 1715vw 1985vw
$\mathrm{Cu(Pn\text{-}Sal)\cdot Co(NO_3)_2\cdot 1.75C_2H_5OH\cdot 0.5H_2O}$	532s* 1215m,br† 1710vw 1985vw
$\mathrm{Cu(Pn\text{-}Sal)\cdot Zn(NO_3)_2}$	520s* 580s,sh 1700vw 1980vw
$\mathrm{2Cu(Pn\text{-}Sal)\cdot Zn(NO_3)_2\cdot 1.5CH_3OH\cdot 2H_2O}$	355vs,sh 533s* 1705w 1685w
$\mathrm{Cu(Pn\text{-}Sal)\cdot CoCl_2\cdot 0.5H_2O}$	565vs† (640sh 660)†vs,dp (1380m,sh 1525s)†dp 2000m,br
$\mathrm{Cu(Pn\text{-}Sal)\cdot ZnCl_2}$	355vs,sh (520* 560sh)s,dp 1700vw
$\mathrm{2Cu(Pn\text{-}Sal)\cdot Cu(ClO_4)_2\cdot 2H_2O}$	365s 505s,br* (1005 1150)*m,br 1945vw
$\mathrm{2Cu(Pn\text{-}Sal)\cdot Cu(ClO_4)_2\cdot en}$	(370vs 420s,sh)dp 583s,br* 730m,sh 1700vw
$\mathrm{Cu(En\text{-}AcAc)}$	365vs,sh (545* 620sh)s,dp 1735w 1950vw
$\mathrm{2Cu(En\text{-}AcAc)\cdot Cu(NO_3)_2\cdot H_2O}$	415s,sh (552s,br 915m,br)* 1740vw

*) vs=very strong s=strong w=weak vw=very weak sh=shoulder br=broad dp=double peak, two bands in succession

*, † =the main *d–d* bands of copper(*) and of metal other than copper (†) which were employed in the discussion of the structure of complexes.

of all the atoms in the complexes.[9,10] For the complexes containing only copper atom as paramagnetic ions, the magnetic moments were calculated per copper atom from the expression $\mu_{\rm eff}=2.83\sqrt{\chi_M/n\cdot T}$ B.M., where n is the number of copper atoms in a molecule. For the complexes in which paramagnetic ions other than copper are present, the magnetic moments were calculated using $\mu_{\rm eff}=2.83\sqrt{\chi_M\cdot T}$ B.M. The temperature-independent paramagnetism associated with the paramagnetic ions was not included in the calculation of $\mu_{\rm eff}$ throughout this work. For binuclear copper(II) complexes with subnormal magnetic moments, the moments observed at room temperature were corrected for minor room temperature variations to those at 25°C, $\mu_{\rm fef}^{25^\circ C}$, by using Bleaney and Bowers' equation assuming $g=2.2$.[11,12] These results are given in Table 3.

III. Diffuse Reflectance Spectral Measurements. The 340—2000 mμ region was investigated on a Hitachi EPS-3T recording spectrophotometer with the use of a reflectance attachment, and optical grade lithium fluoride was used as the standard of light reflectance. Instead of diluting the compounds with the reference material, appropriate absorbancy ranges were selected by controlling the sensitivity knobs on the spectrophotometer. The band maxima of these complexes are recorded in Table 4.

IV. Infrared Spectral Measurements. Infrared spectra were taken in 4000—1200 cm^{-1} region on Low-Polymerized Trifluoroethylene mulls and in 1300—400 cm^{-1} region on Nujol mulls on a Hitachi EPI-G2 model of infrared spectrophotometer. A part of the data are given in Table 5.

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TABLE 5. DATA OF INFRARED SPECTRA OF COMPLEXES**

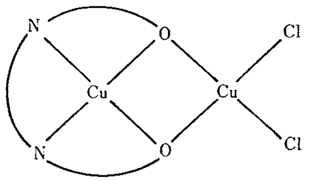
Complexes	Vibrational frequencies, ν, cm^{-1}				
	$\nu_{\mathrm{C-O}}$	$\nu_{\mathrm{NO_3}}$			
Cu(En-Sal)	1528vs				
Cu(En-Sal)$\cdot$CuCl$_2\cdot$0.5CH$_2$OH	1548s,sh 1536s				
Cu(En-Sal)$\cdot$CuCl$_2\cdot$ 0.5C$_2$H$_5$OH	1549s,sh 1538s				
Cu(En-Sal)$\cdot$Cu(NO$_3$)$_2$	1549m	1499s	1295m,br?	1019w 1003m	804w,br
Cu(En-Sal)$\cdot$Cu(NO$_3$)$_2\cdot$ 1.5CH$_3$OH	1554m	1498vs	1296vs,br	1020m 1004s	806m
Cu(En-Sal)$\cdot$Cu(NO$_3$)$_2\cdot$ 1.5CH$_3$OH$\cdot$H$_2$O	1544m	1493m	1288vs,br	1020m 1003w	822vw,br 806w
Cu(En-Sal)$\cdot$Cu(NO$_3$)$_2\cdot$4py	1530s	1496vw 1486w	1296vs,br	1025m 1015s	821m,spw 805v
Cu(En-Sal)$\cdot$Ni(NO$_3$)$_2\cdot$ 2C$_2$H$_5$OH	1552m	1512s,br	1291vs,br	1022m	822w,sp 805w,sp
Cu(En-Sal)$\cdot$Co(NO$_3$)$_2\cdot$1.5C$_2$H$_5$OH$\cdot$ 0.5H$_2$O	1549m	1509vs,br	1295vs,br	1021m,sp	
4Cu(En-Sal)$\cdot$3Zn(NO$_3$)$_2$	1550m 1539m	1490vs	1284vs,br	1020s	810m,sp
Cu(En-Sal)$\cdot$CoCl$_2\cdot$0.5C$_2$H$_5$OH	1550s				
Cu(En-Sal)$\cdot$ZnCl$_2$	1552s				
2Cu(En-Sal)$\cdot$Cu(ClO$_4$)$_2\cdot$ CH$_3$OH$\cdot$2H$_2$O	1549s,br				
2Cu(En-Sal)$\cdot$Ni(ClO$_4$)$_2\cdot$2H$_2$O	1548s				
2Cu(En-Sal)$\cdot$Co(ClO$_4$)$_2\cdot$2H$_2$O	1541s				
2Cu(En-Sal)$\cdot$Zn(ClO$_4$)$_2\cdot$2.5H$_2$O	1550m				
Cu(Pn-Sal)	1530m				
Cu(Pn-Sal)$\cdot$CuCl$_2$	1547m,sh 1531m				
Cu(Pn-Sal)$\cdot$Cu(NO$_3$)$_2$	1551m	1501s	1285vs,br?	1016w 1002m?	804w,br
Cu(Pn-Sal)$\cdot$Ni(NO$_3$)$_2\cdot$2C$_2$H$_5$OH	1552s	$\left.\begin{array}{l}1513\mathrm{s}\\1503\mathrm{s}\end{array}\right]$dp	1289vs,br?	1019s,sp	820w 807m
Cu(Pn-Sal)$\cdot$Co(NO$_3$)$_2\cdot$1.75C$_2$H$_5$OH$\cdot$ 0.5H$_2$O	1551m	1510vs,br	1303vs,br?	1019s,sp	820w 809m
Cu(Pn-Sal)$\cdot$Zn(NO$_3$)$_2$	1550s	1510s, sh?	1294vs,br	1017s,br	810m,sp
2Cu(Pn-Sal)$\cdot$Zn(NO$_3$)$_2\cdot$1.5CH$_3$OH$\cdot$ 2H$_2$O	1544s		1298s,sh?	1017s	826w
Cu(Pn-Sal)$\cdot$CoCl$_2\cdot$0.5H$_2$O	1552m				
Cu(Pn-Sal)$\cdot$ZnCl$_2$	1551m				
2Cu(Pn-Sal)$\cdot$Cu(ClO$_4$)$_2\cdot$2H$_2$O	1550s				
2Cu(Pn-Sal)$\cdot$Cu(ClO$_4$)$_2\cdot$en	1541s				
Cu(En-AcAc)	1113w†				
2Cu(En-AcAc)$\cdot$Cu(NO$_3$)$_2\cdot$H$_2$O	1112w†		1292vs,br	1010s?	815w? 808w? 792m?

** sp=sharp For other symbols, see the footnote of Table 4. The band(†) was assigned to the C–O stretching vibration in chelation by K. Ueno and A. E. Martell (*J. Phys. Chem.*, **59**, 998 (1955)).

Results and Discussion

I. General Discussion of Complex Structures. One of the interesting points of studies of polynuclear complexes would be in the observation of the reaction conditions whose minor difference yields different type of complexes (*cf. e. g.*, C-(f) and -(g), the formation of a binuclear and trinuclear complex by reaction of Cu(Ph-Sal) and Zn(NO$_3$)$_2$). Sometimes, even minor change in the structure of a parent complex or difference in anion part of salts with the same metal gives rise to occurrence of metal exchange reactions; *e. g.*, the copper atom in Cu(Pn-Sal) was exchanged with nickel in ethanol when nickel chloride was employed but no such reaction occurred when nickel nitrate or perchlorate was used under the same reaction condition.

Although the structure of these complexes is unknown at present, Gruber and his co-workers fully discussed probable structures from the consideration of steric hindrance.[7] They proposed the following type of binuclear structure for complexes with the chemical formula, Cu(TDSB)·$CuCl_2$.[*3]



(i)

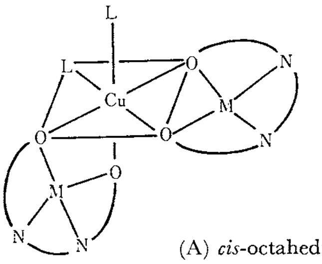
The most powerful supporting evidence for the binuclear structure is the conformation of the magnetic properties of these complexes to the Bleaney and Bowers' equation.[5-7,11]

The complexes with the chemical formula, Cu(TDSB)·$Cu(NO_3)_2$ (*cf.* Table 1) have not been reported by Gruber and co-workers. We assume for these nitrato complexes a binuclear structure of the same type as the chloro complexes based upon the following observations:

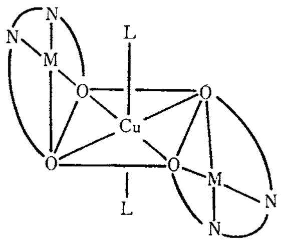
1. The observed subnormal magnetic moments are even lower than those of the corresponding chloro complexes.
2. The appearance of C–O stretching vibration near 1550 cm^{-1}, which is a powerful indication of the presence of bridging phenolic oxygens.[7,13,14]

The properties of Cu(TDSB)·$M(NO_3)_2$(M=Ni, Co and Zn) will be discussed assuming that their structures are the same as those of Cu(TDSB)·$Cu(NO_3)_2$.

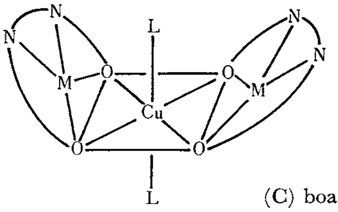
To complexes with formula, 2Cu(TDSB)·$M(ClO_4)_2$(M=Cu, Ni, Co, Zn and other metals), Gruber and co-workers proposed three probable trinuclear structures shown below (ii-A, B and C).



(A) *cis*-octahedral type



(B) chair type



(C) boat type

(ii)

L = solvent molecule attached to the central copper atom

They preferred the *cis*-octahedral type (ii-A). Their recent study of temperature variations of magnetic susceptibilities supported the trinuclear structure for this series of complexes; no appreciable magnetic interaction exists between terminal magnetic ions.[8] However, such magnetochemical studies do not distinguish among a number of probable trinuclear structures.

II. Binuclear Complexes. *A. Infrared Spectra.* a) Band of Bridging Phenolic Oxygen. A shift of the phenolic C–O stretching band of Schiff's base complexes from 1530 cm^{-1} to near 1550 cm^{-1}, can be taken as diagnostic of the formation of polynuclear complexes with bridging phenolic oxygen. Such shift of C–O stretching band toward higher wave numbers was also observed for these complexes.

b) Band of Nitrato Group. The following bands due to coordinately bound nitrato groups[15-22] were observed for Cu(TDSB)·$M(NO_3)_2$,

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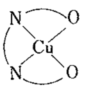
[*3] In this paper, Cu(TDSB) is used for the abbreviation for a copper(II) complex with a tetradentate Schiff's base, and it is schematically expressed as



13) G. E. Batley and D. P. Graddon, *Aust. J. Chem.*, **20**, 877 (1967).

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15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York (1963), pp. 92, 161.

16) B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.*, **1957**, 4222.

17) B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Inorg. Nucl. Chem.*, **8**, 75 (1958).

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19) F. A. Cotton, D. M. L. Goodgame and R. H. Soderberg, *Inorg. Chem.*, **2**, 1162 (1963).

20) R. L. Carlin and M. J. Baker, *J. Chem. Soc.*, **1964**, 5008.

21) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

22) D. E. Billing, A. E. Underhill, D. M. Adams and D. M. Morris, *J. Chem. Soc.* (*A*), **1966**, 902.

ν_4 1490—1510 cm^{-1}

ν_1 1290—1310 cm^{-1}

ν_2 1000—1020 cm^{-1}

ν_6 805— 825 cm^{-1}

The band designation follows Gatehouse and others.[16–18] In most cases, two peaks appeared in the respective absorption regions. This may be due to one of the following:

1. Further splitting of the respective bands may be caused because of a lower symmetry of the nitrato group in complexes possibly due to solid state effects.
2. Two differently bound nitrato groups may be present in the complex. According to Curtis and Curtis,[21] the band (ν_4) of a bi-dentate nitrato region appears at a higher frequency than that of a mono-dentate nitrato group. The other bands (ν_1, ν_2 and ν_6) of a bi-dentate nitrato group appear at lower frequencies compared to those of a mono-dentate nitrato group.

At present infrared spectral study in the NaCl region alone can not distinguish between these possibilities.

The (ν_2) band was taken by Nyholm *et al.* as a criterion of the degree of covalency of metal-nitrate bond.[16,17] A low frequency of this band indicates a high degree of covalency of the bond and *vice versa.* The observed frequency range of the band (ν_2) of the complexes in the present study, near 1000 cm^{-1}, indicates a fairly strong covalent character of the metal-nitrate bond in these complexes.

B. Magnetic Moments and d–d Bands. a) General Consideration for Chloro and Nitrato Complexes. These copper(II) complexes showed, in general, two *d–d* bands which appeared at two distinctly different wavelength regions (*cf.* Fig. 1 and Table 4). These two *d–d* bands are assigned to the two copper ions which are placed in different environments. From the spectrochemical series the *d–d* bands of higher energies of the chloro and nitrato complexes are assigned to Cu_1 and those of lower energies to Cu_2.[23]

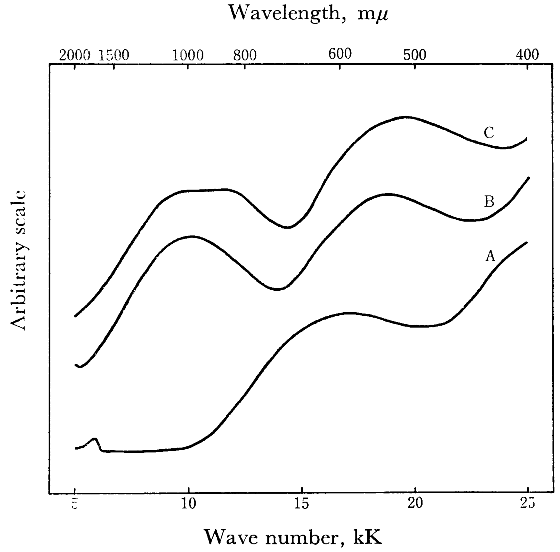
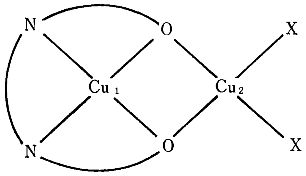
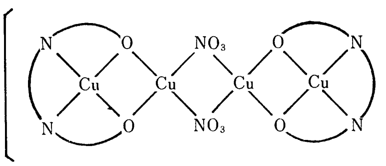


Fig. 1. Reflectance spectra of Cu(En-Sal) (curve A), Cu(En-sal)·$CuCl_2$·0.5C_2H_5OH (curve B) and Cu(En-Sal)·$Cu(NO_3)_2$ (curve C).



(X=Cl and NO_3) (iii)

Gruber's χ-T study have indicated that the chloro complexes should have a dimeric structure. At present, no χ-T data are available for the nitrato complexes. The complexes with the chemical formula, Cu(TDSB)·$Cu(NO_3)_2$, could be higher polymers such as $[Cu(TDSB)\cdot Cu(NO_3)_2]_n (n=2,3,\cdots)$. When $n=2$, one probable structure is as such given in (iv), where outer nitrate groups may be bound weakly to the metal atoms in the complex ion. Even though such a structure is not inconsistent with the infrared spectral data (*cf.* II–A–b), we shall assume a dimeric structure resembling to those of the chloro complexes.



$(NO_3)_2$ (iv)

Gruber and co-workers pointed out that when Cu(TDSB) complexes with metal halides or metal perchlorates, the main ligand field transitions shift to higher energies. This was confirmed in the present study and shown to hold also for complexes with metal nitrates. The main *d–d* band of Cu(En-Sal) appears at a much longer wavelength (590 mμ). This fact is consistent with its dimeric structure in which each copper atom is five coordinated with a pyramidal arrangement.[24] The band of Cu(Pn-Sal) appears at 566 mμ.

On complexing, the main *d–d* band of these Cu(TDSB) shifts towards 540—505 mμ, which is at shorter wavelengths than that of bis(ethylenediamine)copper(II) ions in various ligand field

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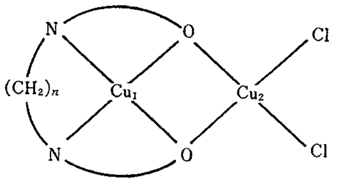
[23] C. K. Jϕrgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, New York, N. Y. (1962), p. 107.

[24] D. Hall and T. N. Waters, *J. Chem. Soc.*, **1960,** 2644.

environments,[25,26] and quite close to that of the copper(II) complexes of planar type.[27-29]

The *d-d* transitions of Cu_I and Cu_2 occur at 515—536 and 945—983 mμ for the chloro complexes and at 506—516 and 855—910 mμ for nitrato complexes respectively. The *d-d* band energy of Cu_2 is greater for nitrato complexes than for chloro complexes in line with their relative positions in the spectrochemical series.[22,23,30]

The magnetic moments of nitrato complexes ranging from 1.25 to 1.45 B. M., are apparently smaller than those of chloro complexes. The empirical rule "higher energies of *d-d* bands-lower magnetic moments" established for dimeric copper(II) halide complexes with pyridine *N*-oxides[3] or salicylideneimines[2,4] where the two copper ions are in essentially the same environment, is apparently also valid for the complex systems of the present study even though each copper ion is placed in a different environment in a dimeric molecule. Gruber and co-workers[7] showed that, for the system,



(n=2, 3,···)

(v)

as n increases, the deviation of the stereochemistry of Cu_I from planarity increases thus bringing about a shift of the *d-d* bands of both Cu_I and Cu_2 to lower energies indicating "mutual influence of complex moieties in a molecule" in the direction $Cu_I \rightarrow Cu_2$. However, the present study indicates that the influence in the reverse direction $Cu_I \leftarrow Cu_2$ also occurs. A shift of *d-d* band of copper(II) complexes to lower energy is correlated with the deviation of stereochemistry of the copper ion from planar to tetrahedral symmetry.[30-33] These are in line with the fact that the more planar the copper(II)-stereochemistry in a binuclear complex, the greater the orbital overlap effective for superexchange interaction between copper ions.[3,4]

b) Cu(TDSB)·$M(NO_3)_2$ (M=Ni, Co and Zn). A binuclear structure of the same type as that for copper(II) nitrate complexes shall be assumed for these nitrato complexes since all showed bridging phenolic oxygen band.[7,13,14] The stereochemistry of M greatly influences the properties of these compounds. Reflectance spectra give reasons for many of these properties.

1) M=Ni(II): Spectral data rule out square-planar, tetrahedral[34-40] and the five coordinated configurations.[34-36,41-44] The spectra best fit those

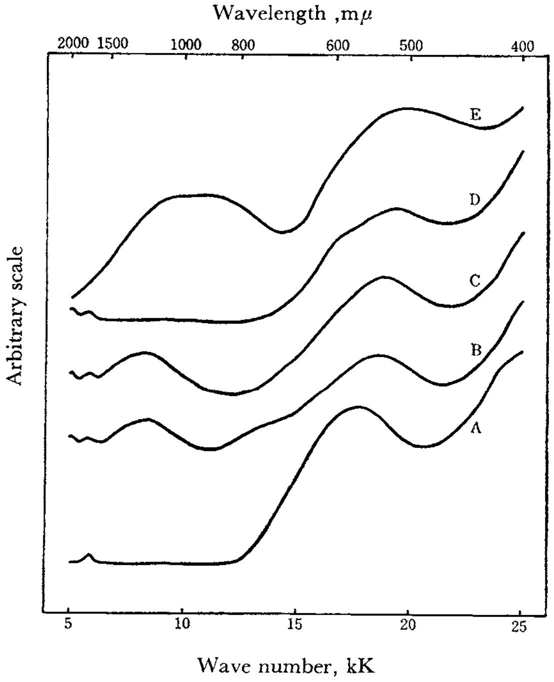


Fig. 2. Reflectance spectra of Cu(Pn-Sal) (curve A), Cu(Pn-Sal)·$Ni(NO_3)_2 \cdot 2C_2H_5OH$ (curve B), Cu(Pn-Sal)·$Co(NO_3)_2 \cdot 1.75C_2H_5OH \cdot 0.5H_2O$ (curve C), Cu(Pn-Sal)·$Zn(NO_3)_2$ (curve D) and Cu(Pn-Sal)·$Cu(NO_3)_2$ (curve E).

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25) K. Sone and S. Utsuno, This Bulletin, **39**, 1813 (1966).

26) I. M. Procter, B. J. Hathaway and P. Nicholls, *J. Chem. Soc.* (*A*), **1968**, 1678.

27) M. Kato, Y. Komuro and K. Sone, *Nippon Kagaku Zasshi*, **78**, 896 (1957).

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31) L. Sacconi and M. Ciampolini, *J. Chem. Soc.*, **1964**, 276.

32) T. P. Cheeseman, D. Hall and T. N. Waters, *J. Chem. Soc.*, *A*, **1966**, 694.

33) W. J. Eilbeck, F. Holmes, C. E. Taylor and A. E. Underhill, *J. Chem. Soc.*, *A*, **1968**, 128.

34) L. Sacconi, *Coordin. Chem. Rev.*, **1**, 192 (1966).

35) S. Yamada, *Kagaku no Ryoiki*, **22**, 681 (1968).

36) S. Yamada, *Coordin. Chem. Rev.*, **1**, 415 (1966).

37) L. Sacconi, *ibid.*, **1**, 126 (1966).

38) D. M. L. Goodgame, M. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, **83**, 4161 (1961).

39) L. Sacconi, P. Paoletti and M. Ciampolini, *ibid.*, **85**, 411 (1963).

40) C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc.*, *A*, **1968**, 237.

41) M. Ciampolini, N. Nardi and G. P. Speroni, *Coordin. Chem. Rev.*, **1**, 222 (1966).

42) L. Sacconi, "Plenary Lectures presented at the 10th International Conference on Coordination Chemistry in September, 1967," Butterworths, London, p. 95.

43) L. Sacconi, P. Nannelli, N. Nardi and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965).

44) M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966).

of Ni(II) complexes with octahedral configurations (*cf.* Fig. 2).[35,45-47] The bands at *ca.* 1200 mμ were assigned to $^3A_{2g}\rightarrow{}^3T_{2g}$ transition and those at 740—750 mμ to $^3A_{2g}\rightarrow{}^3T_{1g}$(F). The characteristic feature of the latter band, which occurs often in double peaks ($^3A_{2g}\rightarrow{}^3T_{1g}$(F) and $^3A_{2g}\rightarrow{}^1E_g$), has become partly hidden by the absorption end of the stronger band of the Cu(TDSB) moiety. The band due to transition, $^3A_{2g}\rightarrow{}^3T_{1g}$ (P), expected at *ca.* 400 mμ, could not be observed, being hidden by the stronger absorption due to *d-d* transition of Cu(TDSB) as well as the strong absorption of charge transfer region.

2) M=Co(II): For Co(II) complexes with nitrato groups, the most probable stereochemical environment of Co(II) is octahedral based on a similar consideration to that for Ni(II).[20,34-36,42,46-60] The bands at *ca.* 1200 mμ were assigned to $^4T_{1g}$(F)$\rightarrow{}^4T_{2g}$(F). The absorption due to transition, $^4T_{1g}$(F) $\rightarrow{}^4T_{1g}$(P) which is expected at *ca.* 500 mμ, was not observed, being hidden by the stronger copper(II) band at 520 mμ.

3) M=Zn(II): Surprisingly the *d-d* band of Cu(TDSB) of this compound appeared at a shorter wavelength (520 mμ) than those for Co(II) and Ni(II) complexes (540—532 mμ). The same trend was observed for Cu(TDSB)·$ZnCl_2$ (*cf.* Table 4 and Fig. 4). The "mutual influence of complex moieties" is out of line here compared to that observed in Cu(TDSB)·CuX_2 (X=Cl and NO_3). It is rather difficult to give a clear-cut explanation for this inconsistency. However, a conceivable mechanism for this conflict may be found in the tetrahedral coordination of the Zn(II) ion and subsequent steric influences. This may decrease the ligand field exerted from neighboring molecules or ions on the fifth or sixth coordination positions of the copper(II) ion in Cu(TDSB).[3,4] Such steric effect might then exceed the effect of the "mutual influence of complex moieties" in a dimeric complex molecule.

c) Other Nitrato Complexes. 1) Cu(En-Sal)·$Cu(NO_3)_2\cdot 1.5CH_3OH\cdot H_2O$: The band ν_{C-O} of this compound appeared at 1544 cm^{-1}. This frequency is somewhat low compared to the band due to bridging phenolic oxygen present in the most binuclear complexes (*ca.* 1550 cm^{-1}).[7,13,14] The *d-d* band appearance of this compound makes it difficult to distinguish between Cu_1 and Cu_2 bands.

The spectral feature of this compound differes from that of most binuclear chloro and nitrato copper(II) complexes but resembles that of the pseudo-tetrahedral binuclear complexes, $[Cu(\overset{1}{O}\cdot C_6H_4\cdot \overset{2}{C}H{=}N{-}R)Cl]_2$ (R=alkyl or aryl groups) (*cf.* Fig. 3).[4,30-33,37,53] The magnetic moment of this compound, 1.75 B.M., is consistent with these facts.

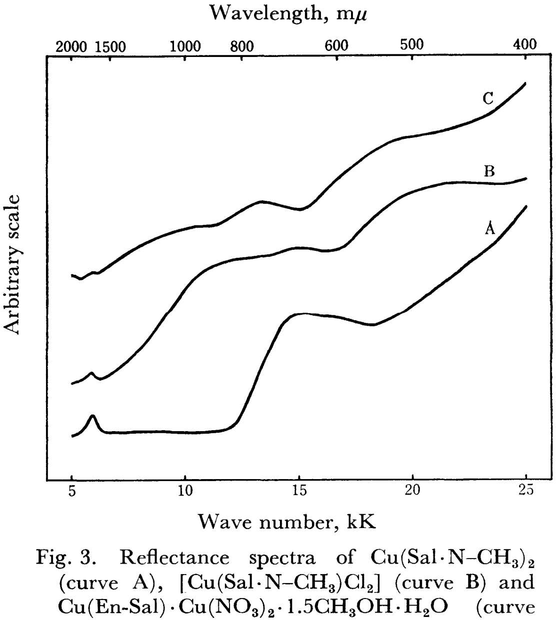

Fig. 3. Reflectance spectra of $Cu(Sal\cdot N{-}CH_3)_2$ (curve A), $[Cu(Sal\cdot N{-}CH_3)Cl_2]$ (curve B) and Cu(En-Sal)·$Cu(NO_3)_2\cdot 1.5CH_3OH\cdot H_2O$ (curve C). $Sal\cdot N{-}CH_3{=}\overset{1}{O}\cdot C_6H_4\cdot \overset{2}{C}H{=}N{-}CH_3$

2) Cu(En-Sal)·$Cu(NO_3)_2\cdot 4Py$: The ν_{C-O} frequency of this compound (1530 cm^{-1}) indicates the absence of bridging phenolic oxygen. The magnetic moment, 1.87 B.M., is consistent with this observation. This compound showed two main *d-d* bands at 585 and 1005 mμ due to two copper(II) ions in different ligand fields.

d) Cu(TDSB)·MCl_2(M=Co and Zn). 1) M=

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[45] R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corporation, New York (1967), pp. 167, 410.

[46] D. W. Meek, R. S. Drago and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

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[48] Ref. 45, p. 411.

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[50] A. Sacco and F. A. Cotton, *ibid.*, **84**, 2043 (1962).

[51] L. Sacconi, M. Ciampolini, F. Maggio and F. P. Cavasino, *ibid.*, **84**, 3246 (1962).

[52] J. A. Bertrand and D. L. Plymale, *Inorg. Chem.*, **3**, 775 (1964).

[53] R. Longhi and R. S. Drago, *ibid.*, **4**, 11 (1965).

[54] D. E. Billing and A. E. Underhill, *J. Chem. Soc.*, *A*, **1968**, 5.

[55] D. E. Billing and A. E. Underhill, *ibid.*, **1968**, 29.

[56] L. Sacconi, M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

[57] L. Sacconi, M. Ciampolini and G. P. Speroni, *J. Amer. Chem. Soc.*, **87**, 3102 (1965).

[58] M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).

[59] L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **88**, 5180 (1966).

[60] S. Yamada and E. Yoshida, This Bulletin, **40**, 1298 (1967).

Co(II): These greyish violet complexes showed three main absorption bands in the 340—2000 mμ region near 565, 660 and 1520 mμ respectively. No peak was observed in the 520 mμ region where most of these complexes showed a broad band due to the *d-d* transition of Cu(TDSB). Instead, a sharp band appeared in the region at *ca.* 565 mμ. This band can not be assigned to the *d-d* band of Cu(TDSB) because of its shape and absorption position (*cf.* Fig. 4). It seems reasonable that in these complexes the band of Cu(TDSB) is hidden under the stronger absorption of Co(II).[50,52] The observed spectra are different from those of octahedral and planar cobalt(II) complexes[35,36,46,47] and are similar to that of tetrahedral Co(II);[34,35,48-55] they have also a resemblance to those of trigonal bipyramidal Co(II).[36,41,42,44,56-60] X-ray analysis of metal complexes often shows them as an intermediate of fundamentally different geometries.[42] An environment of Co(II) for such an intermediate of tetrahedral and trigonal bipyramidal configurations in the presence of ligand A is shown below.

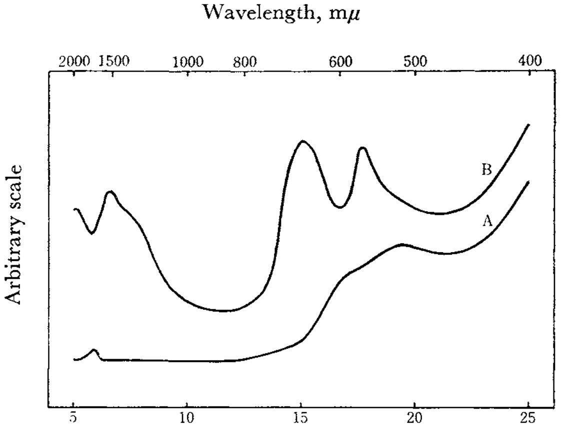
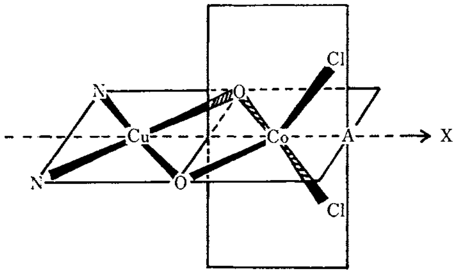


Fig. 4. Reflectance spectra of Cu(En-Sal)·$ZnCl_2$ (curve A) and Cu(En-Sal)·$CoCl_2$·$0.5C_2H_5OH$ (curve B).

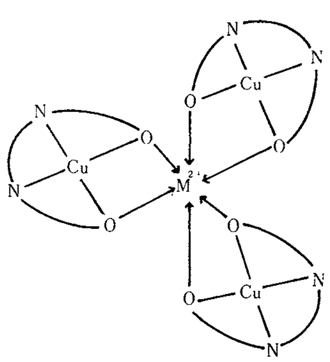


(vi)

Here, A=a solvated molecule or a neighboring molecule or ion which exerts a ligand field on the Co(II) ion in the x direction.

2) M=Zn(II): discussed previously (*cf.* (b)-3).

III. 2Cu(TDSB)·M(ClO_4)$_2$. *A. Formation.*[*4] The ease of formation of trinuclear complexes from metal perchlorate and Cu(TDSB) in alcoholic solution is partly due to the very weak coordinating ability of perchlorate ion. In complex formation from Cu(TDSB) and M(ClO_4)$_2$, the ligands to coordinate to M^{2+} are firstly the complex ligand (Cu(TDSB)) and secondly solvent molecules. In a metal with coordination number of six, two molecules of Cu(TDSB) acting as a bidentate ligand, will occupy four positions, and the remaining two coordinating sites will be occupied by solvent molecules. Steric consideration does not allow three molecules of Cu(TDSB) to attach to one metal without a large amount of strain, *i. e.*, the formation of a tetranuclear complex of the following type does not seem possible for the first transition elements.[7] Such steric condition encountered here is similar to that observed for complex formation of nickel (II) with 2,9-dimethylphenanthroline, where even a large excess of the ligand gave only a bis-complex for steric reason.[61]



(vii)

Recent χ-T studies by Gruber and co-workers supports the trinuclear formation for these perchlorate complexes.[8] For metal chloride or nitrate, the anions have a much greater coordinating ability than the perchlorate ion, and the central metal coordinates with either of the complex ligand and chloride or nitrate ion. Under such conditions, it becomes difficult for one central metal ion to combine with more than a molecule of the complex ligand, leading to the formation of a binuclear complex rather than a trinuclear one. However, in some cases metal nitrates can form trinuclear

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[*4] Metal analysis does not distinguish between the chemical compositions of a binuclear and a trinuclear complex. For instance, per cent of copper is 19.36% for Cu(En-Sal)·Cu(ClO_4)$_2$·$2CH_3OH$(dimer) and 19.26% for 2Cu(En-Sal)·Cu(ClO_4)$_2$·CH_3OH·$2H_2O$(trimer) respectively, practically the same values within the accuracy of our metal analysis, ±0.5%. At the meeting[*1-b] this was pointed out and a trimeric formula was presented for the dimeric one in the proceedings based on Cu and C.H.N. analysis.

61) K. Sone and M. Kato, *Naturwissenschaften*, **45**, 10 (1958).

complexes as in 2Cu(Pn–Sal)·$Zn(NO_3)_2$ or 2Cu(En-AcAc)·$Cu(NO_3)_2$, where nitrate ion has a stronger coordinating ability than chloride ion in line with the spectrochemical series. This suggests that coordinating ability of the anions is not the only factor determining the formation of these polynuclear complexes. Packing or steric effect, or other factors must be considered to be cooperating in this phenomenon.

B. Spectral Features. The spectra of complexes with Cu(En-Sal) are given in Fig. 5. Of all the chloride, nitrate and perchlorate complexes, the *d–d* transitions of Cu(TDSB) always occur at shortest wavelengths when they combine with copper(II) salts. The spectral features of Co(II) and Ni(II) complexes indicate octahedral complexes though the absorptions at wavelengths shorter than 600 mμ are hidden by the stronger absorption of the complex ligand (Cu(TDSB)).

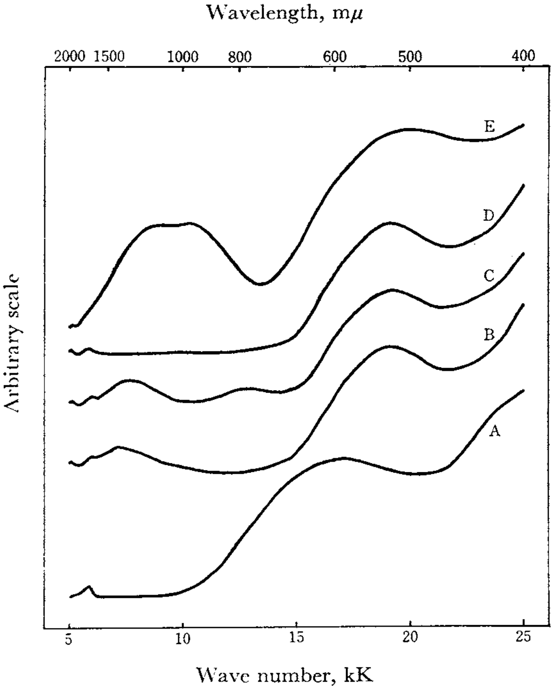

Fig. 5. Reflectance spectra of Cu(En-Sal) (curve A), 2Cu(En-Sal)·$Co(ClO_4)_2 \cdot 2H_2O$ (curve B), 2Cu(En-Sal)·$Ni(ClO_4)_2 \cdot 2H_2O$ (curve C), 2Cu-(En-Sal)·$Zn(ClO_4)_2 \cdot 2.5H_2O$ (curve D) and 2Cu-(En-Sal)·$Cu(ClO_4)_2 \cdot CH_3OH \cdot 2H_2O$ (curve E).

The bands of the central metal ions in perchlorate complexes appear at a lower energy than those of the nitrate complexes. This makes it possible to observe the familiar doublet band of nickel(II) complexes (near 700 mμ) separate from the absorption due to the complex ligand. It is noteworthy that for the perchlorate complexes the *d–d* transitions due to Cu(En-Sal) are in the order from lower to higher energy, Co<Ni<Cu>Zn or Co<Zn<Ni<Cu, the same as the Irving and Williams' sequence for complex stability.[62]

The antiferromagnetic exchange interaction of trinuclear perchlorate complexes, 2Cu(TDSB)·$M(ClO_4)_2$ increases in the order, M=Co<Ni<Cu,[8] is the same as observed for the energy of copper(II) band of Cu(TDSB) in trinuclear complexes of the same type.

C. Some Specific Complexes. a) 2Cu(Pn-Sal)·$Cu(ClO_4)_2 \cdot$en. This compound has a chemical formula in which the two water molecules in 2Cu-(Pn-Sal)·$Cu(ClO_4)_2 \cdot 2H_2O$ are replaced with one ethylenediamine molecule. Such an apparently minor change in the chemical formula, however, gives rise to a great deal of change in its properties. The ethylenediamine compound is greyish green, and the dihydrate compound is violet. The former has only one *d–d* band due to copper(II) at 583 mμ but the dihydrate, as most polynuclear copper(II) complexes of the present study, has two copper(II) bands at greatly different wavelengths, *i.e.*, at *ca.* 520 and 900—1000 mμ respectively (*cf.* Fig. 6). This suggests that in the ethylenediamine complex the copper ions are in practically the same environment whereas in the dihydrate the environment is greatly different for each copper(II) ion. The mechanism by which the two copper(II) ion bands merge into one absorption, and the coordination behavior of ethylenediamine in this complex are under study.[63]

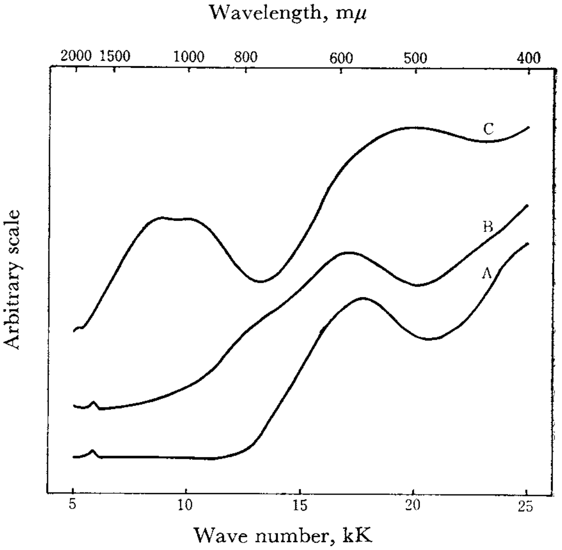

Fig. 6. Reflectance spectra of Cu(Pn-Sal) (curve A), 2Cu(Pn-Sal)·$Cu(ClO_4)_2 \cdot$en (curve B) and 2Cu(Pn-Sal)·$Cu(ClO_4)_2 \cdot 2H_2O$ (curve C).

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[62] F. J. C. Rossotti, "Modern Coordination Chemistry," ed. by L. Lewis and R. G. Wilkins, Interscience Publishers, New York, N. Y. (1960), p. 1.

[63] Ref. 15, p. 186.

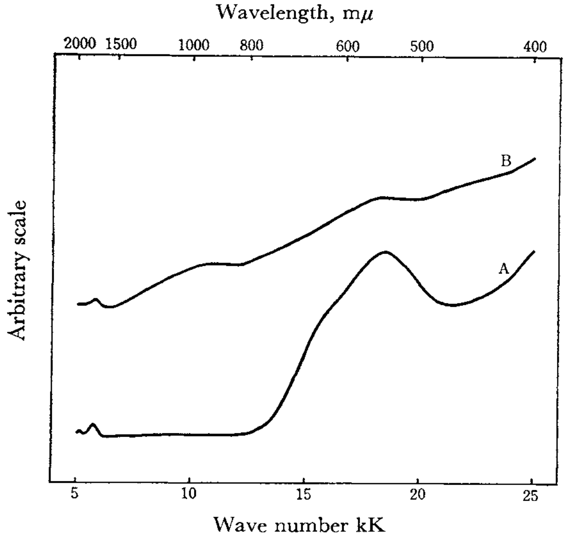

Fig. 7. Reflectance spectra of Cu(En-AcAc) (curve A) and 2Cu(En-AcAc)·Cu$(NO_3)_2$·H_2O (curve B).

b) 2Cu(En-AcAc)·Cu$(NO_3)_2$·H_2O. The spectral features of this compound indicate a pseudo-tetrahedral copper(II) complex (*cf.* Fig. 7).[30-33,37] The structures of Cu(En-Sal)[24] and Cu(En-AcAc)[64] determined by X-ray analysis indicate that the steric hindrance due to these complex ligands in the formation of the polynuclear complexes is greater in Cu(En-AcAc) than in Cu(En-Sal). The magnetic moment, 1.76 B.M. suggests the existence of an antiferromagnetic interaction in this compound.[3,4]

One area of the further development of the present study will involve the systematic research for the conditions under which even minor changes in the structure of the parent compound lead to the formation of different type of polynuclear complexes, bi-nuclear or tri-nuclear ones, in the cooperation of the specific property of the respective anion of the metal salt employed in the preparation.

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64) D. Hall, A. D. Rae and T. N. Waters, *J. Chem. Soc.*, **1963**, 5897.