Synthesis and Characterization of Trinuclear Schiff-base Complexes containing Sulphur Dioxide or Hydrogensulphite Ions as Bridging Groups. Crystal Structure of $[Zn\{(\mu\text{-}CH_3CO_2)(salpd\text{-}\mu\text{-}O,O')Cu\}_2]$ [salpd = propane-1,3-diylbis(salicylideneiminate)]†

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Trinuclear complexes of general formulas $[MCu_2(CH_3CO_2)_2(salpd)_2]$ (M = Mg^{II}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II}) and $[MNi_2(CH_3CO_2)_2(salpd)_2]$ (M = Mg^{II}, Mn^{II}, Co^{II}, or Ni^{II}) were prepared, where H_2salpd represents propene-1,3-diylbis(salicylideneimine). Further reactions of the complexes of the former series with sulphur dioxide yielded $[MCu_2(CH_3CO_2SO_2)_2(salpd)_2]$ (M = Mg^{II}, Mn^{II}, Co^{II}, or Ni^{II}) and $[Cu_3(HSO_3)_2(salpd)_2(H_2O)_2]$. Cryomagnetic measurements (77.4—295 K) have shown that a weak or negligible antiferromagnetic spin coupling ($J = -46$ to 0 cm^{-1}) is operating between the terminal and central metal ions in the complexes except for $[Cu_3(HSO_3)(salpd)_2(H_2O)_2]$ which showed a strong antiferromagnetic coupling ($J = -186$ cm^{-1}) between neighbouring copper(II) ions. *X*-Ray crystal analysis was carried out for $[Zn\{(\mu\text{-}CH_3CO_2)(salpd\text{-}\mu\text{-}O,O')Cu\}_2]$. It crystallizes in the monoclinic space group $P2_1/a$ with $a = 16.228(5)$, $b = 11.971(2)$, $c = 9.239(3)$ Å, $\beta = 100.15(3)°$, $Z = 2$, and $R = -0.0887$. The complex consists of a linear Cu^{II}–Zn^{II}–Cu^{II} trinuclear unit which has an inversion centre. The Cu^{II} and Zn^{II} are bridged by the two phenolate oxygens of the salpd and the oxygens of the acetate ion.

In a previous paper[1] we reported the syntheses, structures, and properties of mixed-valent trinuclear cobalt complexes $[Co^{II}(\mu\text{-}SO_3)_2(\mu\text{-}L)_2Co^{III}{}_2(ROH)_2]$ (L = Schiff base dianion, R = alkyl). It was demonstrated by the *X*-ray crystal analysis for one of these complexes that the cobalt ions are bridged by phenolic oxygens of the Schiff base, and by sulphite ions through the sulphur and oxygen atoms.[1] Of particular interest from the standpoint of studies of geometry and magnetism are new complexes with other spin systems, prepared by the replacement of the cobalt ions in the above trinuclear complexes by other transition-metal ions.

In this study, series of linear heterometal trinuclear complexes with general formulas $[MCu_2(CH_3CO_2)_2(salpd)_2]$ [M = Mg^{II}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, or Zn^{II}; salpd = propane-1,3-diylbis(salicylideneiminate)] and $[MNi_2(CH_3CO_2)_2(salpd)_2]$ (M = Mg^{II}, Mn^{II}, Co^{II}, or Ni^{II}) have been prepared. The structural and magnetic characterization of these complexes should be interesting in view of the elucidation of the correlation between bridging structure and spin coupling. These complexes react further with sulphur dioxide to form a new series of complexes which may be formulated as $[MCu_2(CH_3CO_2SO_2)_2(salpd)_2]$ (M = Mg^{II}, Mn^{II}, Co^{II}, or Ni^{II}) and $[Cu_3(HSO_3)_2(salpd)_2(H_2O)_2]$ and should contain novel bridging systems.

Experimental

Preparation of the Starting Materials.—The Schiff-base ligand H_2salpd and [M(salpd)] (M = Cu^{II} or Ni^{II}) were prepared by the method previously reported.[2]

Trinuclear Schiff-base Complexes with Acetate Bridges.—$[MgCu_2(CH_3CO_2)_2(salpd)_2]\cdot 0.5H_2O$ (**1a**). The complex $[Cu(salpd)]\cdot 0.33H_2O$ (1.10 g, 3.14 mmol) was added with stirring to a methanol (50 cm^3) solution containing $Mg(CH_3CO_2)_2\cdot 4H_2O$ (0.37 g, 1.71 mmol) at room temperature. After several minutes a green precipitate began to appear in a green solution. The mixture was allowed to stand for 5 h. The green product (1.25 g) was collected on a sintered glass filter, washed with ethanol and diethyl ether, and dried at 50 °C under reduced pressure for 30 min.

$[MnCu_2(CH_3CO_2)_2(salpd)_2]\cdot 0.5H_2O$ (**2a**). This compound was obtained as a green powder (1.30 g) from $Mn(CH_3CO_2)_2\cdot 4H_2O$ (0.42 g, 1.71 mmol) and $[Cu(salpd)]\cdot 0.33H_2O$ (1.10 g, 3.14 mmol) by a procedure similar to that above except that the reaction was conducted in a closed vessel with bubbling N_2.

$[CoCu_2(CH_3CO_2)_2(salpd)_2]\cdot H_2O$ (**3a**). This complex was obtained as a green powder by using $Co(CH_3CO_2)_2\cdot 4H_2O$ (0.43 g, 1.71 mmol) and $[Cu(salpd)]\cdot 0.33H_2O$ (1.00 g, 2.86 mmol) in a manner similar to that described for the preparation of (**2a**).

Compounds (**4a**)—(**6a**) were obtained by procedures similar to that for (**1a**) except for the use of $Ni(CH_3CO_2)_2\cdot 4H_2O$

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† Di-μ-acetato-1:2κ²*O*:*O′*; 2:3κ²*O″*:*O‴*-bis[μ-propane-1,3-diylbis-(salicylideneiminato)]-1κ²*N*,*N′*; 1:2κ²*O*:*O′*; 2:3κ²*O″*:*O‴*; 3κ²*N″*,*N‴*-1,3-dicopper(II)-2-zinc(II).

Supplementary data available (No. SUP 56793, 7 pp.): magnetic susceptibilities and moments. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Non-S.I. units employed: B.M. ≈ 9.27 × 10^{-24} J T^{-1}, mmHg ≈ 133 Pa.

(0.43 g, 1.71 mmol), $Cu(CH_3CO_2)_2\cdot H_2O$ (0.35 g, 1.74 mmol), and $Zn(CH_3CO_2)_2\cdot 2H_2O$ (0.38 g, 1.71 mmol) instead of $Mg(CH_3CO_2)_2\cdot 4H_2O$: $[NiCu_2(CH_3CO_2)_2(salpd)_2]\cdot 0.5H_2O$ (**4a**), starting with $[Cu(salpd)]\cdot 0.33H_2O$ (2.86 mmol), yield 0.90 g; $[Cu_3(CH_3CO_2)_2(salpd)_2]\cdot 1.5H_2O$ (**5a**), yield 1.20 g; $[Zn\{(\mu\text{-}CH_3CO_2)(salpd\text{-}\mu\text{-}O,O')Cu\}_2]$ (**6a**), yield 1.20 g.

Preparation of a Single Crystal of the Trinuclear Complex.—A mixture of $Zn(CH_3CO_2)_2\cdot 2H_2O$ (0.08 g, 0.36 mmol) and $[Cu(salpd)]\cdot 0.33H_2O$ (0.20 g, 0.57 mmol) in methanol (60 cm^3) was mechanically shaken for 40 min for complete dissolution. The single crystal used for X-ray analysis was grown by allowing this solution to stand for 2 weeks in the dark.

$[MgNi_2(CH_3CO_2)_2(salpd)_2]\cdot 0.5H_2O$ (**7a**).—The complex $[Ni(salpd)]\cdot 1.33H_2O$ (1.00 g, 2.75 mmol) was added with stirring to a methanol (50 cm^3) solution containing $Mg(CH_3CO_2)_2\cdot 4H_2O$ at room temperature. The mixture was stirred further for 24 h. The yellowish green compound (1.10 g) formed was collected by filtration, washed with methanol and ether, and dried at 50 °C under reduced pressure for 40 min.

Compounds (**8a**)—(**10a**) were obtained by similar procedures except for the use of $Mn(CH_3CO_2)_2\cdot 4H_2O$ (0.42 g, 1.71 mmol), $Co(CH_3CO_2)_2\cdot 4H_2O$ (0.42 g, 1.69 mmol), and $Ni(CH_3CO_2)_2\cdot 4H_2O$ (0.43 g, 1.73 mmol) instead of $Mg(CH_3CO_2)_2\cdot 4H_2O$: $[MnNi_2(CH_3CO_2)_2(salpd)_2]\cdot 0.5H_2O$ (**8a**), yield 1.10 g; $[CoNi_2(CH_3CO_2)_2(salpd)_2]\cdot H_2O$ (**9a**), yield 1.10 g; and $[Ni_3(CH_3CO_2)_2(salpd)_2]\cdot 0.33H_2O$ (**10a**), yield 1.10 g.

Products of Reaction of Complexes (**1a**)—(**5a**) *with* SO_2.—$[MgCu_2(CH_3CO_2SO_2)_2(salpd)_2]$ (**1b**). Triethylamine (0.40 g, 3.95 mmol) was added with stirring to a methanol (50 cm^3) solution of $Mg(CH_3CO_2)_2\cdot 4H_2O$ (0.36 g, 1.68 mmol) at room temperature. After removal of the air in the vessel by passing nitrogen gas, $[Cu(salpd)]\cdot 0.33H_2O$ (1.00 g, 2.86 mmol) was added to the mixture. In a few minutes a green precipitate [probably (**1a**)] began to appear. The reaction mixture was stirred further for 5 h in the closed system. The nitrogen gas of the vessel was replaced with sulphur dioxide, and the reaction mixture was stirred with ice-cooling for 2 d. During this procedure the mixture became transparent dark green, and the greyish green products were formed. The product deposited was collected on a sintered glass filter, washed with methanol and ether, and dried at 50 °C under reduced pressure for 50 min. Yield; 0.95 g.

The synthetic procedures for the analogues (**2b**)—(**4b**) were the same except for the use of $Mn(CH_3CO_2)_2\cdot 4H_2O$ (0.42 g, 1.71 mmol), $Co(CH_3CO_2)_2\cdot 4H_2O$ (0.41 g, 1.66 mmol), or $Ni(CH_3CO_2)_2\cdot 4H_2O$ (0.40 g, 1.61 mmol) instead of $Mg(CH_3CO_2)_2\cdot 4H_2O$: $[MnCu_2(CH_3CO_2SO_2)_2(salpd)_2]$ (**2b**), yield 1.15 g; $[CoCu_2(CH_3CO_2SO_2)_2(salpd)_2]$ (**3b**), yield 1.20 g; $[NiCu_2(CH_3CO_2SO_2)_2(salpd)_2]$ (**4b**), yield 0.85 g.

$[Cu_3(HSO_3)_2(salpd)_2(H_2O)_2]$ (**5b**).—When dry sulphur dioxide was bubbled through an ethanol solution (50 cm^3, 99.5%) containing $Cu(CH_3CO_2)_2\cdot H_2O$ (0.41 g, 2.05 mmol) and triethylamine (0.50 g, 4.94 mmol) in an ice-bath for 19 h the solution turned light green. To this solution was added $[Cu(salpd)]\cdot 0.33H_2O$ (1.00 g, 2.86 mmol) with cooling in an ice-bath, and the resulting mixture was exposed to a dry sulphur dioxide atmosphere with stirring in a closed system for *ca.* 14 h at room temperature. The yellowish green products (1.35 g) deposited were collected on a sintered glass filter, washed with methanol and ether, and dried at 60 °C under reduced pressure for 40 min.

The colours, yields, and elemental analytical data are given in Table 1.

Measurements.—Elemental analyses of carbon, hydrogen, and nitrogen were carried out at the Elemental Analysis Service Center of Kyushu University and at the Microanalytical Laboratory of Osaka City University. The sulphur content was determined gravimetrically as barium sulphate. Metal analyses were carried out with a Model 170-50 A Hitachi atomic absorption flame spectrophotometer.

Diffuse reflectance spectra were obtained with a Hitachi Model 200—10 spectrophotometer, i.r. spectra with a Shimadzu FTIR-4200 Fourier-transform spectrophotometer on KBr disks. Magnetic susceptibilities were measured by the Faraday method in the range 77.4—295 K using a Shimadzu MB-2 Faraday balance. The apparatus was calibrated by using $[Cr(NH_3)_6]Cl_3$. Diamagnetic corrections were carried out by using Pascal's constants. The effective molar magnetic moments were calculated by the equation $\mu_{eff} = 2.828\sqrt{\chi_A T}$.

X-*Ray Crystallography.*—The diffraction data for a single crystal of $[Zn\{(\mu\text{-}CH_3CO_2)(salpd\text{-}\mu\text{-}O,O')Cu\}_2]$ were obtained on a Rigaku AFC-5 four-circle diffractometer, using graphite-monochromatized Mo-K_α radiation at 24 ± 1 °C. The scan mode was θ—2θ with scan speed 4° min^{-1}, scan width $(1.2 + 0.35 \tan \theta)°$, 2θ range 2.5—55°, and octant measured $+h$, $+k$, $\pm l$. Intensities of standard reflections monitored showed no changes during data collection. Reflections were corrected for Lorentz-polarization, but not for absorption.

Crystal data. $C_{38}H_{38}Cu_2N_4O_8Zn$, $M = 869.414$, monoclinic system, space group $P2_1/a$, $a = 16.228(5)$, $b = 11.971(2)$, $c = 9.239(3)$ Å, $\beta = 100.15(3)°$, $U = 1766.7(9)$ Å^3, $Z = 2$, $D_c = 1.634$ g cm^{-3}, μ(Mo-K_α) = 19.3 cm^{-1}, crystal dimensions 0.3 × 0.4 × 0.4 mm, number of reflections with $|F_o| > 3\sigma|F_c|$ 2048.

Structure determination. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method, in which the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and unit weights were adopted for all the reflections. The hydrogen atoms were located on the Fourier difference map and refined. The positions of non-hydrogen atoms were refined using anisotropic thermal parameters, and those of hydrogen atoms were refined using isotropic thermal parameters, giving $R = 0.0887$, $R' = 0.1091$. The final Fourier difference synthesis showed several peaks around the zinc and copper atoms (1.2 e Å^{-3}). The calculations were carried out by use of the UNICS III computer program system[3] on a FACOM M 780 computer at the Computer Center of Kyushu University. Atomic scattering factors were taken from ref. 4. The final positional parameters are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Results and Discussion

Structure of $[Zn\{(\mu\text{-}CH_3CO_2)(salpd\text{-}\mu\text{-}O,O')Cu\}_2]$.—The molecular structure with atomic numbering is shown in Figure 1(*a*) and (*b*), bond lengths and angles in Table 3. The complex consists of a trinuclear unit which has an inversion centre. The co-ordination geometry of the terminal copper(II) ions is square pyramidal.

The donor atoms of salpd occupy the four equatorial positions of the terminal copper(II) ion with bond distances 1.964(9)—1.988(12) Å, and the apical position is occupied by one of the oxygens of the acetate ion [2.165(9) Å]. The atoms Cu, N(1), C(8), C(9), C(10), and N(2) form a six-membered chelate ring of chair form. The zinc ion is located at the centre of inversion, and its co-ordination geometry can be described as a distorted octahedron. The four bridging phenolate oxygens are co-ordinated in a plane [Zn–O(1) 2.097(9), Zn–O(2) 2.126(8) Å]

Table 1. Colours, yields, and elemental analyses of the trinuclear complexes

Complex	Colour	Yield (%)	Analysis (%)					
			C	H	Cu	M	N	Ni
(1a)	Green	94.7	54.15	4.85	15.10	2.60 (Mg)	6.50	
			(54.40)	(4.70)	(15.15)	(2.90)	(6.70)	
(2a)	Green	95.2	52.35	4.65	14.80	6.25 (Mn)	6.25	
			(52.50)	(4.50)	(14.60)	(6.30)	(6.45)	
(3a)	Green	71.4	51.55	4.75	13.95	6.70 (Co)	6.10	
			(51.70)	(4.55)	(14.40)	(6.70)	(6.35)	
(4a)	Yellowish green	72.1	52.15	4.60	14.00	6.80 (Ni)	6.40	
			(52.25)	(4.50)	(14.55)	(6.70)	(6.40)	
(5a)	Yellowish green	93.8	50.80	4.50	21.70		6.00	
			(50.90)	(4.60)	(21.25)		(6.25)	
(6a)	Yellowish green	85.7	52.05	4.45	14.40	7.65 (Zn)	6.30	
			52.30[b]	4.30[b]			6.40[b]	
			(52.40)	(4.40)	(14.60)	(7.50)	(6.45)	
(7a)	Yellowish green	96.5	55.05	4.80		2.90 (Mg)	6.70	14.15
			(55.05)	(4.75)		(2.95)	(6.75)	(14.15)
(8a)	Yellowish green	93.2	53.35	4.55		6.35 (Mn)	6.50	13.70
			(53.05)	(4.55)		(6.40)	(6.50)	(13.65)
(9a)	Yellowish green	91.7	52.00	4.45		6.70 (Co)	6.50	13.75
			(52.30)	(4.60)		(6.75)	(6.40)	(13.45)
(10a)	Yellowish green	93.9	53.05	4.65			6.45	20.20
			(53.05)	(4.55)			(6.50)	(20.45)
(1b)	Greyish green	69.3	47.60	4.20	13.80	2.15 (Mg)	6.45	6.85
			(47.65)	(4.00)	(13.25)	(2.55)	(5.85)	(6.70)
(2b)	Greyish green	84.6	46.20	4.10	13.30	5.50 (Mn)	5.95	6.50
			(46.15)	(3.85)	(12.85)	(5.55)	(5.65)	(6.50)
(3b)	Greyish green	84.6	46.35	4.05	12.20	5.75 (Co)	6.15	5.75
			(45.95)	(3.85)	(12.80)	(5.95)	(5.65)	(6.45)
(4b)	Greyish green	59.9	46.30	4.10	13.20	5.65 (Ni)	6.10	6.35
			(46.00)	(3.85)	(12.80)	(5.90)	(5.65)	(6.45)
(5b)	Yellowish green	99.3	43.50	3.75	19.80		5.85	6.55
			(43.00)	(4.05)	(20.10)		(5.90)	(6.75)

[a] Calculated values in parentheses. [b] Value for single crystals.

and the remaining co-ordination sites are occupied by the bridging acetate oxygens [Zn–O(3) 2.102(9) Å].

The dihedral angle between the plane formed by the Cu, O(1), and O(2) atoms and that formed by Cu, O(4), O(3), and Zn is 92.5°. The terminal copper(II) ion deviates from the O(1), N(1), N(2), and O(2) plane by 0.19 Å towards O(4), whereas the deviations of the atoms forming the basal plane fall in the range ± 0.13 Å, indicating that this plane is considerably distorted.

In the course of the preparation of the SO_2-containing complexes, trinuclear complexes of the general formulas $[MCu_2(CH_3CO_2)_2(salpd)_2]$ and $[MNi_2(CH_3CO_2)_2(salpd)_2]$ were obtained from mixtures of [Cu(salpd)] or [Ni(salpd)] and $M(CH_3CO_2)_2 \cdot nH_2O$ in 2:1 molar ratio in methanol or ethanol, where M = Mg^{II}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} or Zn^{II} and n = 1 or 4. Of these trinuclear complexes only $[Zn\{(\mu\text{-}CH_3CO_2)(\text{salpd-}\mu\text{-}O,O')Cu\}_2]$ formed single crystals suitable for *X*-ray analysis. The chemical formulas of complexes (**1a**)—(**10a**) cited in the Experimental section were based on the elemental analyses and the analogy to the structures of $[Zn\{(\mu\text{-}CH_3CO_2)(\text{salpd-}\mu\text{-}O,O')Cu\}_2]$ and of previously reported complexes[5] which have been demonstrated by *X*-ray analyses.

The diffuse reflectance spectra of powder samples of complexes (**1a**)—(**6a**) are given in Figure 2. The band at about 16 000 cm^{-1} [except for (**5a**)] is assignable to the *d–d* transition of the terminal copper(II) ions, because in this region the intensities of the *d–d* bands of the central MO_6 moiety are much weaker than that of Cu^{II} when M = Mn^{II}, Co^{II}, and Ni^{II}, and there is no absorption when M = Mg^{II} or Zn.[6a] The spectra of complexes (**1a**)—(**6a**), except for (**5a**), closely resemble each other, suggesting that their co-ordination structures are similar to that of (**6a**).

The i.r. bands of the complexes are listed in Table 4. The band in the 1541—1555 cm^{-1} region may be assigned to the skeletal vibrations related to the bridging phenolic oxygen of the Schiff-base ligand; this band is known to shift to higher frequency when the phenolic oxygen bridges between two metal ions.[1,7–12] All the complexes (**1a**)—(**10a**) exhibit $\nu_{asym}(CO_2)$ in the 1590—1560 cm^{-1} region and $\nu_{sym}(CO_2)$ in the 1430—1418 cm^{-1} region for acetate. The close resemblance of the shape and the position of these bands, except for (**5a**), suggests similar co-ordination modes of the salpd and acetate ions. For (**5a**) the band splits into two at 1541 and 1555 cm^{-1}, suggesting the presence of two different bridging modes of the phenoxide groups. A similar band splitting was observed for a linear tetranuclear complex $[Cu(\text{salpd-}\mu\text{-}O,O')(\mu\text{-}CH_3CO_2)Cu(\mu\text{-}CH_3O)_2\text{-}Cu(\mu\text{-}CH_3CO_2)(\text{salpd-}\mu\text{-}O,O')Cu]$.[5] The X-ray structural analysis revealed that this phenomenon stems from an unsymmetrical bridging of phenoxide oxygens between terminal and inner copper ions, *i.e.* one of the phenoxide oxygens is linked to the inner copper at the equatorial site, the other at the axial site. As for the acetate bridge, one of the oxygens co-ordinates to the terminal copper(II) at the apical position, and the other to the neighbouring copper at an equatorial position. Based on these facts the structure of Figure 3 is assumed for (**5a**) as the most probable one.

The temperature variation of the magnetic susceptibilities (χ_M per mol) and magnetic moments (μ_{eff} per trinuclear unit) of the complexes in the temperature range 77.4—295 K are given in Figures 4 and 5. Complexes (**1a**), (**6a**) and (**7a**) whose central metal ion is diamagnetic (Mg^{II} or Zn^{II}) are expected to have negligible or no magnetic interaction because of the large separation

Table 2. Fractional atomic co-ordinates ($\times 10^4$) of [Zn{(μ-CH_3CO_2)(salpd-μ-*O,O′*)Cu}$_2$] with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Zn	0	0	0
Cu	652(1)	1 803(1)	2 224(2)
O(1)	−295(6)	756(8)	1 892(10)
O(2)	1 153(6)	703(8)	1 060(11)
O(3)	−341(6)	1 488(8)	−1 159(10)
O(4)	68(6)	2 864(8)	435(10)
N(1)	226(8)	2 493(11)	3 896(12)
N(2)	1 706(8)	2 685(10)	2 488(13)
C(1)	−727(9)	402(12)	2 911(15)
C(2)	−1 215(9)	−579(12)	2 594(16)
C(3)	−1 689(9)	−964(14)	3 608(17)
C(4)	−1 646(10)	−426(15)	4 915(18)
C(5)	−1 204(10)	523(15)	5 247(17)
C(6)	−714(9)	958(13)	4 225(15)
C(7)	−275(10)	1 999(13)	4 608(16)
C(8)	510(13)	3 619(16)	4 482(22)
C(9)	1 398(11)	3 904(15)	4 464(20)
C(10)	1 639(12)	3 849(12)	2 990(20)
C(11)	2 405(10)	2 323(14)	2 224(18)
C(12)	2 577(9)	1 212(13)	1 731(15)
C(13)	3 419(10)	933(17)	1 763(20)
C(14)	3 642(11)	−98(19)	1 358(20)
C(15)	3 036(11)	−883(15)	883(18)
C(16)	2 204(10)	−620(14)	802(19)
C(17)	1 949(9)	432(12)	1 181(16)
C(18)	−321(8)	2 482(12)	−758(15)
C(19)	−873(11)	3 293(14)	−1 786(18)

Table 3. Selected bond lengths (Å) and angles (°) of [Zn{(μ-CH_3CO_2)(salpd-μ-*O,O′*)Cu}$_2$] with e.s.d.s in parentheses

Cu ··· Zn	3.038(2)	Zn–O(1)	2.097(9)
Zn–O(2)	2.126(8)	Zn–O(3)	2.102(9)
Cu–O(1)	1.964(9)	Cu–O(2)	1.964(10)
Cu–N(1)	1.981(12)	Cu–N(2)	1.988(12)
Cu–O(4)	2.165(9)	O(2)–C(17)	1.32(2)
O(1)–C(1)	1.34(2)	O(3)–C(18)	1.25(2)
O(4)–C(18)	1.26(2)	N(1)–C(8)	1.50(2)
N(1)–C(7)	1.28(2)	N(2)–C(10)	1.48(2)
N(2)–C(11)	1.28(2)		
Cu–O(1)–Zn	96.7(4)	Cu–O(2)–Zn	95.8(4)
Cu–O(4)–C(18)	122.7(9)	Zn–O(3)–Zn	131.8(9)
O(3)–C(18)–O(14)	126.2(13)	O(1)–Zn–O(2)	75.9(3)
O(3)–Zn–O(1)	88.8(4)	O(3)–Zn–O(2)	91.7(3)
O(1)–Cu–O(2)	82.8(4)	O(1)–Cu–N(1)	90.9(4)
N(1)–Cu–N(2)	95.3(5)	O(2)–Cu–N(2)	89.6(4)
O(4)–Cu–O(1)	91.7(3)	O(4)–Cu–O(2)	98.2(4)
O(4)–Cu–N(1)	100.6(4)	O(4)–Cu–N(2)	91.9(4)

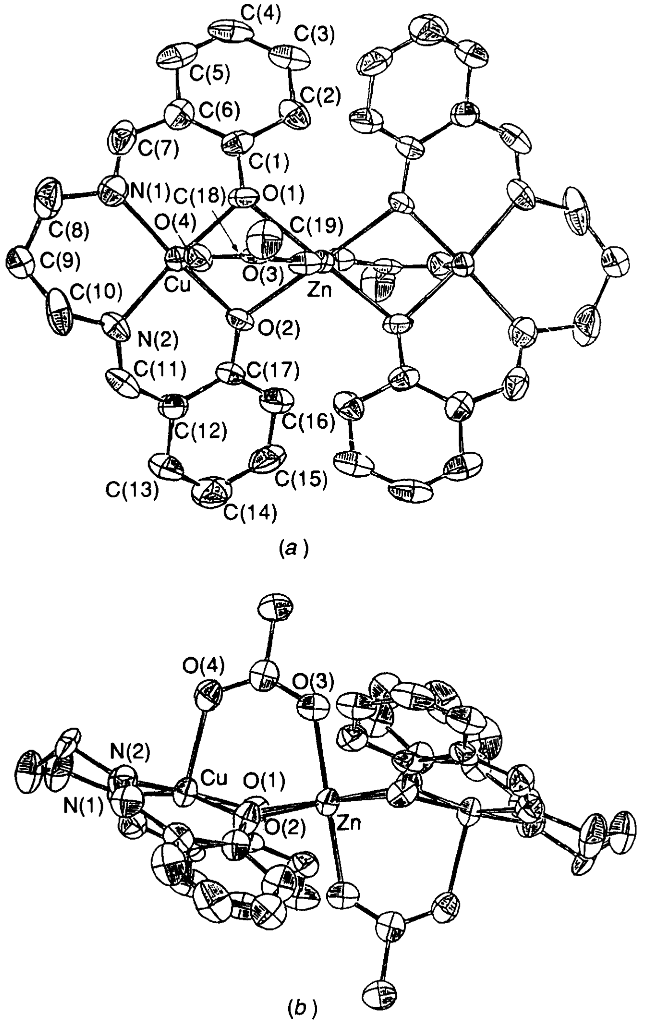


Figure 1. Molecular structure (*a*) and side view (*b*) of [Zn{(μ-CH_3CO_2)(salpd-μ-*O,O′*)Cu}$_2$] drawn by ORTEP

Table 4. I.r. data (cm^{-1}) for the trinuclear complexes (**1a**)—(**10a**)

Complex	Skeletal	ν(CO_2) asym	ν(CO_2) sym
(**1a**)	1 549vs	1 588vs	1 418s
(**2a**)	1 550vs	1 566vs	1 426s
(**3a**)	1 549vs	1 580vs	1 426s
(**4a**)	1 550vs	1 566vs	1 426s
(**5a**)	1 542vs 1 550vs	1 560vs	1 425s
(**6a**)	1 550vs	1 582vs	1 430m
(**7a**)	1 549vs	1 589vs	1 430s
(**8a**)	1 549vs	1 576vs	1 424s
(**9a**)	1 549vs	1 579vs	1 426s
(**10a**)	1 547vs	1 578vs	1 422vs

The skeletal vibrations of [Cu(salpd)] and [Ni(salpd)] were observed at 1538 and 1535 cm^{-1}, respectively.

between the terminal metal ions. In fact, the effective magnetic moments per copper or nickel ion are 2.00, 2.06, and 3.35, respectively at 295 K, which fall in the range usually found for mononuclear copper(II) or nickel(II) complexes at room temperature. The temperature dependences of the magnetic moments of the complexes are very small, and it appears that the magnetic susceptibilities follow the Curie–Weiss law $\chi_A = \alpha(T - \theta)^{-1}$ with a negative θ value, where the Weiss constants θ (α in parentheses) for (**1a**), (**6a**), and (**7a**) are −22(0.5), −32(0.6), and −15(1.5) K, respectively. Therefore, these data suggest the scarcity of magnetic interaction between the terminal metal ions.

Complex (**8a**) has a manganese(II) ion as the central metal, but the temperature variation of the magnetic moment is very small as in the cases of (**1a**), (**6a**) and (**7a**); *i.e.* the μ_{eff} per mol of (**8a**) at 77.4 and 294 K are 7.95 and 7.92, respectively. Since magnetic moments for monomeric high-spin nickel(II) (octahedral) and manganese(II) (octahedral) complexes are known to fall in the ranges 2.9—3.5, and 5.7—6.0 B.M., respectively, the magnetic moment for a non-spin-coupled

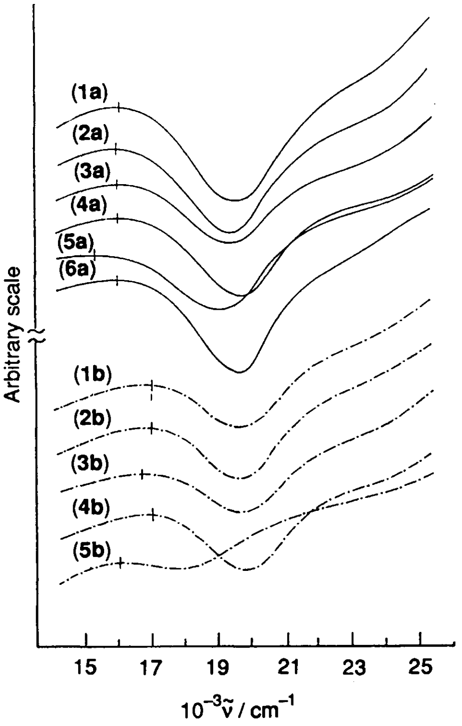


Figure 2. Reflection spectra of the complexes

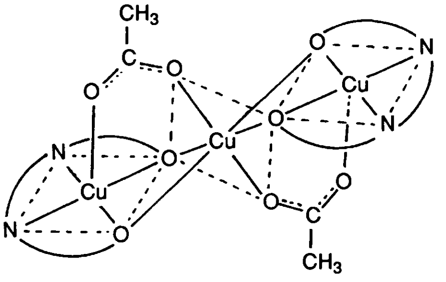


Figure 3. Possible structure for complex (**5a**)

Ni^{II}(S = 1)–Mn^{II}(S = $\frac{5}{2}$)–Ni^{II}(S = 1) system is estimated at 7.02—7.78 B.M. from the equation $\mu_M{}^2 = \Sigma\mu_i{}^2$.[10] The observed magnetic moment of (**8a**) at room temperature is very close to the estimated upper limit of 7.78 B.M. Accordingly, it is presumed that the Ni^{II} and Mn^{II} in (**8a**) are in high-spin states, and that there is negligible or no magnetic interaction between any pair of metal atoms.

For the other complexes the temperature dependences of the magnetic moments are not negligible; the moments apparently decrease with lowering of temperature, as seen from Figures 4 and 5. We have analysed the magnetic susceptibility data of the trinuclear complexes using the Van Vleck equation based on the Heisenberg model assuming a linear trinuclear system. For the Cu(S = $\frac{1}{2}$)–M^{II}–Cu(S = $\frac{1}{2}$) system, the equations based on $H = -2J(S_{Cu2}{\cdot}S_{M1} + S_{Cu3}{\cdot}S_{M1})$ can be found in the literature, where M = Mn(S = $\frac{5}{2}$),[8b,11] Co(S = $\frac{3}{2}$),[8b,10] Ni(S = 1),[8b] and Cu(S = $\frac{1}{2}$).[8b] Analogous formulas for the Ni^{II}–M^{II}–Ni^{II} system based on $H = -2J(S_{Ni2}{\cdot}S_{M1} + S_{Ni3}{\cdot}S_{M1})$ have been worked out as shown below, and used for the analysis of the relevant data.

For M = Mn(S = $\frac{5}{2}$) (**8a**):

$$\chi_M = (Ng^2\beta^2/4kT)(A/B) + N\alpha \qquad (1)$$

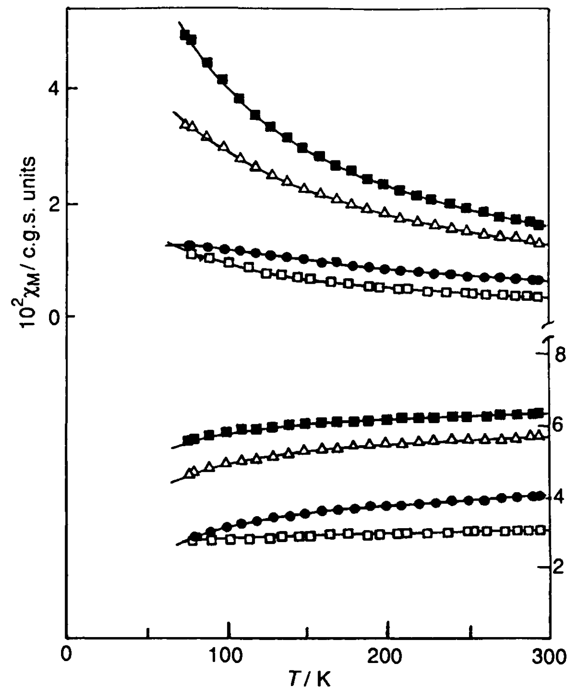


Figure 4. Temperature variations of magnetic susceptibilities and effective magnetic moments. Complexes: (■) (**2a**), (△) (**3a**), (●) (**4a**), and (□) (**5a**)

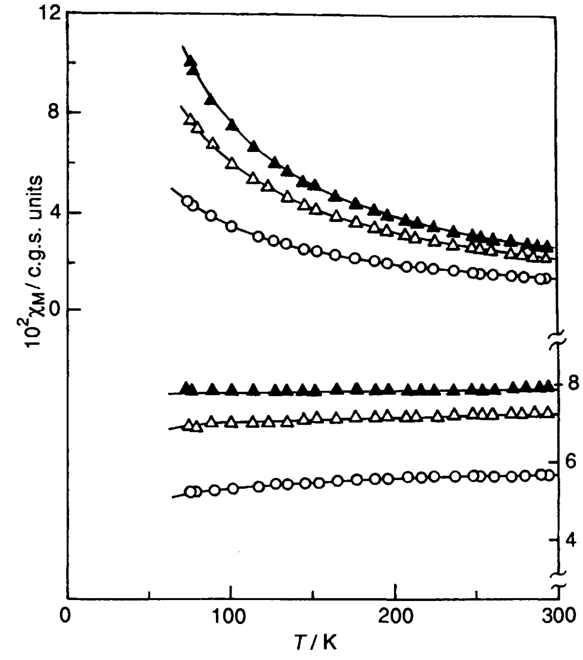


Figure 5. Temperature variations of magnetic susceptibilities and effective magnetic moments. Complexes: (▲) (**8a**), (△) (**9a**), and (○) (**10a**)

$$A = 10 + 165\exp(17J/kT) + 84\exp(8J/kT) + 35\exp(J/kT) + 10\exp(-4J/kT) + \exp(-7J/kT) + 84\exp(12J/kT) + 35\exp(5J/kT) + 35\exp(7J/kT)$$

$$B = 2 + 5\exp(17J/kT) + 4\exp(8J/kT) + 3\exp(J/kT) + 2\exp(-4J/kT) + \exp(-7J/kT) + 4\exp(12J/kT) + 3\exp(5J/kT) + 3\exp(7J/kT)$$

$N\alpha$ = 480 × 10^{-6} c.g.s. (480/4π S.I.) units mol^{-1}

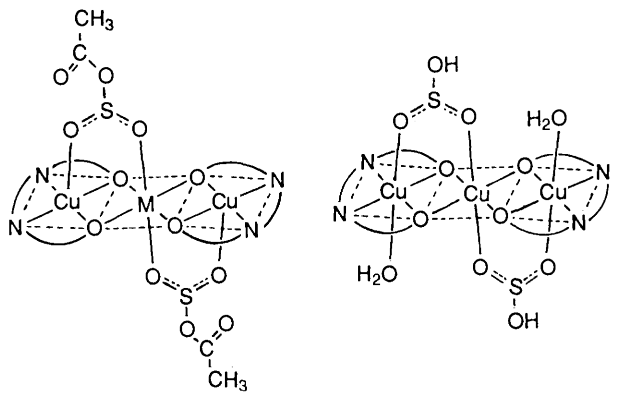
Table 5. Magnetic parameters of the complexes[a]

Complex	$-J$/cm^{-1}	g	10^6 $N\alpha$/c.g.s. units[b]
(2a)	10	2.06	120
(3a)	16	2.57	500
(4a)	32	2.33	350
(5a)	19	2.02	180
(8a)	0	2.20	480
(9a)	2	2.58	700
(10a)	6	2.29	690
(2b)	16	2.14	120
(3b)	23	2.57	500
(4b)	46	2.39	350
(5b)	186	2.25	180

[a] The J' value between the terminal metal ions is estimated at 0 cm^{-1}. C.g.s. unit = ($10^6/4\pi$) S.I. unit. [b] Values of $N\alpha$ from ref. 8*b* [**(2a)**—**(5a)**, **(2b)**—**(5b)**]; ref. 6*b* [**(8a)**—**(10a)**].

Table 6. I.r. data (cm^{-1}) for the trinuclear complexes **(1b)**—**(5b)**

Complex	Skeletal	$\nu(CO_2)$	ν(S–O)			
(1b)	1 553vs	1 599vs	1 075vs 1 036vs	968s	654vs	
(2b)	1 555vs	1 599vs	1 073vs 1 022vs	965s	650s	
(3b)	1 553vs	1 599vs	1 074vs 1 015s	961s	652s	
(4b)	1 553vs	1 599vs	1 073vs 1 017s	963s	652s	
		ν(S—O)(HSO_3^-)				
(5b)	1 559s	1 148vs	1 057s 1 038m	853s	617s	585s



(*a*) (*b*)

Figure 6. Possible structures of the trinuclear complexes: (*a*) **(1b)**—**(4b)** and (*b*) **(5b)**

For M = Co($S = \frac{3}{2}$) **(9a)**:

$$\chi_M = (Ng^2\beta^2/4kT)(A/B) + N\alpha \qquad (2)$$

$$A = 10 + 84\exp(8J/kT) + 35\exp(J/kT) + 10\exp(-4J/kT) + \exp(-7J/kT) + 35\exp(5J/kT) + \exp(-3J/kT) + 10\exp(2J/kT)$$

$$B = 2 + 4\exp(8J/kT) + 3\exp(J/kT) + 2\exp(-4J/kT) + \exp(-7J/kT) + 3\exp(5J/kT) + \exp(-3J/kT) + 2\exp(2J/kT)$$

$$N\alpha = 700 \times 10^{-6}\ \text{c.g.s.}\ (700/4\pi\ \text{S.I.})\ \text{units mol}^{-1}$$

The equation for M = Ni(S = 1) was given in ref. 13. Here, J is the exchange integral between the terminal and central metal ions, the exchange interaction between the two terminal copper(II) ions being assumed to be zero, and the other symbols have their usual meanings. The values of the temperature-independent paramagnetism ($N\alpha$) were adopted from the value of Gruber *et al.*[8b] for the MCu_2 system and from the value of Figgis[6b] for the MNi_2 system, where M = Mn^{II}, Co^{II}, or Ni^{II}.

Application of these equations to the present trinuclear complexes resulted in good fits to the experimental data as seen in Figures 4 and 5, where the solid lines are theoretical curves obtained with the best-fit parameters summarized in Table 5. The J values of **(2a)**—**(5a)** are in the range -10 to -32 cm^{-1}, indicating the operation of antiferromagnetic interactions. In the Ni^{II}–M^{II}–Ni^{II} system the J values of the complexes **(8a)**, **(9a)**, and **(10a)** are zero, -2, and -6 cm^{-1}, respectively, which are small compared with those of **(2a)**—**(5a)**.

It is to be noted that complex **(5a)** could be obtained by the reaction of [Cu(salpd)] with $Cu(CH_3CO_2)_2 \cdot H_2O$, only when ethanol was used as solvent. We have already reported that in the preparation of **(5a)** the use of methanol instead of ethanol caused preferential formation of the linear tetranuclear copper(II) complex [Cu(salpd-μ-*O,O'*)(μ-CH_3CO_2)Cu(μ-CH_3O)$_2$Cu(μ-CH_3CO_2)(salpd-μ-*O,O'*)Cu].[5] The reaction of the complexes **(1a)**—**(4a)** suspended in methanol with sulphur dioxide yielded green powdered compounds **(1b)**—**(4b)** with general formula $[MCu_2(CH_3CO_2SO_2)_2(salpd)_2]$. The compound **(5b)** with the formula $[Cu_3(HSO_3)_2(salpd)_2(H_2O)_2]$ was formed as a yellowish green powder by the reaction of **(5a)** suspended in methanol or ethanol with sulphur dioxide. No sulphur dioxide was lost when the SO_2-containing complexes were kept at 40—60 °C under reduced pressure (7.6 mmHg) for 40—50 min. In the case of **(3b)**, no weight loss was detected even after heating at 140—147 °C for 3 h under reduced pressure (0.05 mmHg), and there was no difference in the i.r. spectra measured before and after heating. These complexes could not be recrystallized because they were insoluble or hardly soluble in common organic and inorganic solvents. All attempts to obtain $[Cu_3(CH_3CO_2SO_2)_2(salpd)_2]$ resulted in the formation of **(5b)** which contains HSO_3^- and H_2O instead of SO_2 and $CH_3CO_2^-$. I.r. data for these complexes are given in Table 6. The strong bands of **(1b)**—**(4b)** in the regions 1 015—1 075, 961—968, and 650—654 cm^{-1} are assignable to vibrations related to the bonded SO_2 because of the absence of these bands in the spectra of the corresponding **(a)**-type complexes. Complex **(5b)** shows strong or medium bands in the regions 1 038—1 057, 853, 617, and 585 cm^{-1} which originate from the co-ordinated HSO_3^-.

For complexes **(1b)**—**(4b)**, $\nu_{asym}(CO_2)$ is shifted to higher frequency by 11—33 cm^{-1} compared with the original complexes **(1a)**—**(4a)**. This suggests that the bonding mode of the acetate ion has changed from bidentate to unidentate upon incorporation of the SO_2 molecule. Although it is difficult at present to determine the bonding mode of sulphur dioxide in **(1b)**—**(4b)** based only on the above data, one of the possible structures for these complexes is shown in Figure 6(*a*). Since sulphur dioxide and the acetate ion are a Lewis acid and base, respectively, they may combine to form the $CH_3CO_2SO_2^-$ ion[14] in the case of **(1b)**—**(4b)**. On the other hand, **(5b)** is assumed to have the structure given in Figure 6(*b*). For this compound the phenolic ν(CO) was observed at 1559 cm^{-1} and showed no splitting, suggesting that the bridging phenolic oxygens are all equivalent.

The absorption bands of complexes **(1b)**—**(4b)** (Figure 2) in the region *ca.* 16 000—17 000 cm^{-1} are assignable to the *d–d* transitions of terminal copper(II) ions for the same reason as that for the **(a)**-type complexes. The spectra closely resemble

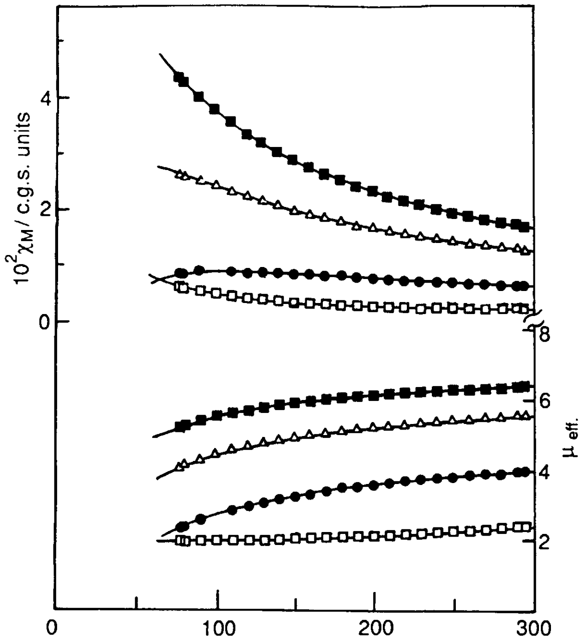


Figure 7. Temperature variations of magnetic susceptibilities and effective magnetic moments. Complexes: (■) (**2b**), (△) (**3b**), (●) (**4b**), and (□) (**5b**)

each other, suggesting that the complexes have similar co-ordination structures. On the other hand, the spectrum of (**5b**) is different from those of (**1b**)—(**4b**), and its *d–d* band position is close to those of the (**a**)-type complexes.

Temperature variations of the magnetic susceptibilities (χ_M per mol) and magnetic moments (μ_{eff} per trinuclear unit) of the complexes in the temperature range 77.4—295 K are shown in Figure 7. The magnetic susceptibility data for (**1b**)—(**5b**) were analysed by applying the same equations employed for the corresponding (**a**)-type complexes. It is evident that an anti-ferromagnetic spin-exchange interaction operates between the terminal and central metal ions in complexes (**2b**)—(**5b**). The exchange integrals ($J = -16$ to -46 cm^{-1}) of complexes (**2b**)—(**4b**) with a bridging Schiff base and $CH_3CO_2SO_2^-$ are significantly larger than those ($J = -10$ to -32 cm^{-1}) of the corresponding parent complexes (**1a**)—(**4a**). On the other hand, (**5b**) exhibits a strong antiferromagnetic spin-exchange interaction ($J = -186$ cm^{-1}) between the adjacent copper(II) ions. The remarkable difference between the values for (**5a**) and (**5b**) may be attributed to the difference in the bridging structures [*cf.* Figures 3 and 6(*b*)].

Acknowledgements

We wish to express our gratitude to Professors Kosho Katsura and Yosei Uehara for their continued interest and support, and to Mr. Mamoru Miyagi for help with the preparation of the trinuclear nickel(II) complexes.

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Received 10*th April* 1990; *Paper* 0/01603I