Oxalate-Bridged Dinuclear Cr(III)–M(II) (M = Cu, Ni, Co, Fe, Mn) Complexes: Synthesis, Structure, and Magnetism

Masaaki Ohba, Hiroko Tamaki, Naohide Matsumoto, and Hisashi Ōkawa*

Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki,
Higashi-ku, Fukuoka 812, Japan

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The following oxalate-bridged heterodinuclear Cr(III)–M(II) (M = Cu, Ni, Co, Fe, Mn) complexes have been synthesized: [Cr(salen)(ox)Cu(acpy)] (**1**) (salen = *N,N'*-ethylenebis(salicylideneaminate), ox^{2-} = oxalate ion, acpy = *N*-acetylacetonylidene-*N*-(2-pyridylethyl)aminate) and [Cr(salen)(ox)M(taea)](BPh_4) (M = Ni (**2**), Co (**3**), Fe (**4**), Mn (**5**)) (taea = tris(2-aminoethyl)amine). The [Cr(salen)(ox)Cu(acpy)]2DMF·MeOH (**1'**) complex crystallizes in the monoclinic system of the space group $P2_1/n$ with $a = 16.429(6)$ Å, $b = 25.303(14)$ Å, $c = 10.191(4)$ Å, $\beta = 109.78(2)°$, $V = 3986(3)$ Å^3, and $Z = 4$. The refinement converges with $R = 0.079$ and $R_w = 0.071$ based on 3327 reflections with $|F_o| \geq 3\sigma(|F_o|)$. The complex has an oxalate-bridged dinuclear Cr(III)–Cu(II) core with a Cr···Cu distance of 5.482(3) Å. The Cr(III) has a *cis*-β octahedral geometry with the tetradentate salen in the folded form and a bidentate oxalate group. The geometry around the Cu(II) ion is square-pyramidal with the three donor atoms of acpy and one of the oxalate oxygens at the basal plane and the other oxygen of the oxalate group at the apex. Magnetic investigations of **1–5** in the 4.2–300 K temperature range reveal a ferromagnetic interaction between the Cr(III) and M(II) ions for all the complexes. On the basis of the spin Hamiltonian, $\hat{H} = -2JS_{Cr}\cdot S_M$, the values for the spin coupling constant *J* were estimated to be +2.8, +4.6, +1.3, +0.8, and +0.5 cm^{-1} for **1–5**, respectively. The relative magnitude of the *J* values is explained by the σ- and π-pathways through the oxalate bridge. The correlation between the *J* values of **1–5** and the phase-transition temperatures, T_C, of the ferromagnetic $\{NBu_4[MCr(ox)_3]\}_x$ (M = Cu, Ni, Co, Fe, Mn) is discussed based on Heisenberg's ferromagnet model.

Introduction

The design of ferromagnetic materials based on metal complexes has been one of the most stimulating subjects in the field of inorganic chemistry.[1–5] The method generally adopted involves preparing a ferromagnetic or ferrimagnetic chain and assembling the chain so as to achieve a three-dimensional ferromagnetic ordering.[2–4] Using this principle, three types of complex-based ferromagnets have been reported: (1) one-dimensional charge-transfer complexes such as $\{[Fe(Me_5Cp)_2]^+[TCNE]^-\}_n$ (Me_5Cp = pentamethylcyclopentadienyl, TCNE = tetracyanoethylene),[1] (2) one-dimensional bimetallic systems such as $\{MnCu(pbaOH)(H_2O)_3\}_n$ ($pbaOH^{4-}$ = 2-hydroxy-1,3-propylenebis(oxamate) anion)[2] and $MnCu(obbz)\cdot H_2O$ (obbz = oxamidobis(benzoato),[3] and (3) a one-dimensional radical-Mn(II) complex $\{Mn(hfa)_2(NITR)\}_n$ (hfa^- = hexafluoroacetylacetonate ion, NITR = 2-*R*-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide).[4]

Recently, we have proposed another synthetic method for complex-based ferromagnets[6] using a D_3-symmetric η^3-complex as a building block to provide a three-dimensional network structure in a one-pot reaction. In a previous study we adopted tris(oxalato)chromate(III), $[Cr(ox)_3]^{3-}$, as such a building block to prepare a series of heterometal assemblies $\{NBu_4[MCr(ox)_3]\}_x$ (NBu_4^+ = tetrabutylammonium ion; M(II) = Mn, Fe, Co, Ni, Cu, Zn).[6] Those assemblies except for that of M = Zn were found to be ferromagnets showing a magnetic phase-transition (T_C) at 6–14 K. Furthermore, a series of heterometal assemblies $\{NBu_4[MFe(ox)_3]\}_x$ (M(II) = Mn, Fe, Ni, Zn)[7] were prepared using tris(oxalato)ferrate(III), $[Fe(ox)_3]^{3-}$, as the building block, and the assemblies with M = Fe and Ni were found to be ferrimagnets with T_N = 43 and 26 K, respectively. Thus, the magnetic phase-transition temperature (T_C or T_N) of the heterometal assemblies, $\{NBu_4[M^{II}M'^{III}(ox)_3]\}_x$, is variable depending upon the combination of the metal ion pair M(II) and M'(III).

In order to develop fundamental bases for the ferro- or ferrimagnets of high T_C or T_N, it is very important to clarify the factors contributing to the magnetic phase-transition temperature of $\{NBu_4[MM'(ox)_3]\}_x$. In this study we have prepared oxo-

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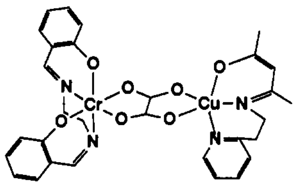
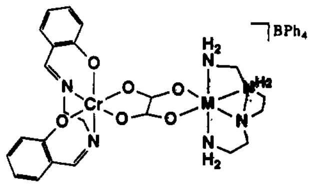
Chart I



(1)



M^{II}=Ni (2), Co(3), Fe (4), Mn(5)

bridged dinuclear Cr(III)–M(II) complexes, [Cr(salen)(ox)Cu(acpy)] (**1**) (salen = N,N′-ethylenebis(salicylideneaminate); acpy = *N*-acetylacetonylidene-*N*-(2-pyridylethyl)aminate) and [Cr(salen)(ox)M(taea)](BPh_4) (M = Ni (**2**), Co (**3**), Fe (**4**), Mn (**5**)) (taea = tris(2-aminoethyl)amine), as the nearest components of {NBu_4[$MCr(ox)_3$]}$_x$. The chemical structures of **1**–**5** are shown in Chart I. The crystal structure of [Cr(salen)(ox)Cu(acpy)]·2DMF·MeOH (**1′**) was determined by the single-crystal X-ray method and the magnetic properties of **1**–**5** were studied in the temperature range 4.2–300 K to determine their spin-exchange integrals *J*. The correlation between the *J* values of **1**–**5** and the phase-transition temperature T_C of {NBu_4[$MCr(ox)_3$]}$_x$ (M = Cu, Ni, Co, Fe, Mn) was discussed based on Heisenberg's ferromagnet model.

Experimental Section

Physical Measurements. Elemental analyses of C, H, and N were obtained from the Service Center of Elemental Analysis of Kyushu University. Metal (Cr, Cu, Ni, Co, Fe, and Mn) analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Infrared spectra were measured using KBr disks with a JASCO IR-810 spectrophotometer. Electronic spectra were recorded by the diffuse-reflectance technique on a Shimadzu multipurpose spectrophotometer, Model MPS-2000. Magnetic susceptibilities were measured with a HOXAN HSM-D SQUID susceptometer in the temperature range 4.2–100 K and with a Faraday balance in the temperature range 80–300 K. Calibrations were made with $Mn(NH_4)_2(SO_4)_2{\cdot}6H_2O$ for the SQUID susceptometer and with $[Ni(en)_3]S_2O_3$ for the Faraday balance.[8] Diamagnetic corrections were made using Pascal's constants.[9] Effective magnetic moments were calculated from the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility corrected for the diamagnetism of the constituting atoms.

Synthesis of Complexes. The Cr(III) component complex [Hpip][Cr(salen)(ox)] (Hpip⁺ = piperidinium cation) was prepared according to the literature method.[10] The Cu(II) component complex [Cu(acpy)H_2O]ClO_4 was obtained as green crystals from the reaction of $Cu(ClO_4)_2{\cdot}6H_2O$, Hacpy, and triethylamine with a mole ratio of 1:1:1 in methanol.[11]

[Cr(salen)(ox)Cu(acpy)]·1.5H₂O (1). [Hpip][Cr(salen)(ox)] (250 mg, 0.5 mmol) was dissolved in a methanol–water mixture (ca. 3:1 in volume, 30 cm³). This solution was added to a methanol solution (20 cm³) of [Cu(acpy)(H_2O)]ClO_4 (190 mg, 0.5 mmol) at room temperature in order to immediately precipitate a dark green crystalline material. It was collected by suction filtration, washed with methanol, and dried *in vacuo* over P_2O_5. It was recrystallized from dichloromethane at room temperature. *Caution*! All the operations should be carried out without heating to avoid contamination with byproducts such as {Cu(ox)}$_n$. Yield: 525 mg (78%). Anal. Calcd for $C_{30}H_{32}CrCuN_4O_{8.5}$: C, 51.47; H, 4.61; N, 8.00; Cr, 7.43; Cu, 9.08. Found: C, 51.71; H, 4.44; N, 8.09; Cr, 7.10; Cu, 8.79. IR data [ν/cm⁻¹] on KBr disks: 3460 (br), 1665, 1625, 1600, 1445, 1320, 1295, 780, 772.

[Cr(salen)(ox)Ni(taea)](BPh₄)·MeOH (2). [Hpip][Cr(salen)(ox)] (250 mg, 0.5 mmol) was dissolved in a methanol–water mixture (ca. 3:1 in volume, 30 cm³). This solution was added to a methanol solution (20 cm³) of $NiCl_2{\cdot}6H_2O$ (120 mg, 0.5 mmol) and taea (73 mg, 0.5 mmol) at room temperature. Next $NaBPh_4$ (170 mg, 0.5 mmol) was added to this mixture to immediately precipitate a brown crystalline material. It was collected by suction filtration, washed with methanol, and dried *in vacuo* over P_2O_5. Yield: 420 mg (88%). Anal. Calcd for $C_{49}H_{56}BCrN_6NiO_7$: C, 61.15; H, 5.86; N, 8.73; Cr, 5.40; Ni, 6.10. Found: C, 61.10; H, 5.67; N, 8.58; Cr, 5.15; Ni, 6.01. IR data [ν/cm⁻¹] on KBr disks: 3430 (br), 3330, 3260, 3050, 1665, 1625, 1600, 1445, 795, 760, 735, 705.

[Cr(salen)(ox)Co(taea)](BPh₄)·MeOH (3). This complex was prepared as light brown microcrystals in a manner similar to that of **2**, except that $CoCl_2{\cdot}6H_2O$ was used instead of $NiCl_2{\cdot}6H_2O$. All operations of the synthetic procedure were carried out under an atmosphere of argon. Yield: 365 mg (76%). Anal. Calcd for $C_{49}H_{56}BCrCoN_6O_7$: C, 61.13; H, 5.86; N, 8.73; Cr, 5.40; Co, 6.12. Found: C, 60.96; H, 5.69 N, 8.82; Cr, 5.34; Co, 6.21. IR data [ν/cm⁻¹] on KBr disks: 3430 (br), 3320, 3260, 3040, 1660, 1620, 1590, 1440, 795, 760, 735, 710.

[Cr(salen)(ox)Fe(taea)](BPh₄)·MeOH (4). This complex was prepared as ocher microcrystals in a manner similar to that of **3**, except that $FeCl_2{\cdot}4H_2O$ was used instead of $CoCl_2{\cdot}6H_2O$. Yield: 345 mg (72%). Anal. Calcd for $C_{49}H_{56}BCrFeN_6O_7$: C, 61.33; H, 5.88; N, 8.76; Cr, 5.40; Fe, 5.82. Found: C, 61.13; H, 5.70 N, 8.81; Cr, 5.27; Fe, 5.78. IR data [ν/cm⁻¹] on KBr disks: 3420 (br), 3330, 3260, 3045, 1660, 1620, 1600, 1445, 800, 765, 735, 710.

[Cr(salen)(ox)Mn(taea)](BPh₄) (5). This complex was prepared as brown microcrystals in a manner similar to that of **3**, except that $MnCl_2{\cdot}4H_2O$ was used instead of $CoCl_2{\cdot}6H_2O$. Yield: 360 mg (72%). Anal. Calcd for $C_{48}H_{52}BCrMnN_6O_6$: C, 62.21; H, 5.66; N, 9.07; Cr, 5.61; Mn, 5.92. Found: C, 62.11; H, 5.71 N, 8.97; Cr, 5.17; Mn, 6.11. IR data [ν/cm⁻¹] on KBr disks: 3340, 3260, 3050, 1660, 1620, 1600, 1450, 800, 760, 735, 710.

X-ray Structural Analysis of [Cr(salen)(ox)Cu(acpy)]·2DMF·MeOH (1′). Single crystals of **1′** were obtained from the crude product of **1**, which might contain methanol, after it was dissolved in DMF and the solution was diffused with 2-propanol. A crystal sealed in a glass capillary tube was used for the X-ray diffraction measurements. X-ray data were collected on a Rigaku Denki AFC-5 four-circle automated diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å) at 20 ± 1 °C. The cell parameters were determined from 25 reflections in the 2θ range 20° ≤ 2θ ≤ 30°. For the intensity data collections, the ω–2θ scan mode was used at the scan rate of 3° min⁻¹ and the scan width was (1.2 + 0.35 tan θ)°. The octant measured was +*h*,+*k*,±*l*. Standard reflections were observed every 100 reflections and showed good stabilities. The intensity data were corrected for Lorentz and polarization effects, but no absorption correction was applied. A total of 3327 reflections with $|F_o| \geq 3\sigma(|F_o|)$ were used for the structure determination.

The structure was solved by the direct method and refined by the block-diagonal least-squares method. Reliability factors were defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$, where the weights were taken as $w = 1/\sigma(|F_o|)$. The atomic scattering factors were taken from ref 12. The contributions of hydrogen atoms bound to carbons were introduced in the calculated positions but were not refined and included in the last cycle of the least-squares calculations. The final difference Fourier synthesis was featureless. All the computations were carried out on a FACOM M-1800/20 computer at the Computer Center of Kyushu University using the UNICS III program system.[13] The final positional parameters of non-hydrogen atoms with their estimated standard deviations are listed in Table I.

Results and Discussion

Synthesis. Two synthetic methods are generally available for producing discrete heterodinuclear complexes: (1) the use of heterodinucleating ligands with two dissimilar coordination sites with respect to either the coordination geometry or the ligand field strength and (2) the use of "complex ligands" that can function as ligands to a second metal ion. Our purpose was to obtain heterodinuclear Cr(III)–ox–M(II) complexes; therefore, the latter synthetic approach was adopted and [Cr(salen)(ox)]⁻ was chosen as the complex ligand. This complex is significantly inert toward metal substitution and can function as a bidentate ligand through the outer oxygens of its ox group.

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Table I. Positional and Isotropic Equivalent Thermal Parameters of Selected Atoms for [Cr(salen)(ox)Cu(acpy)]·2DMF·MeOH

atom	*x*	*y*	*z*	$B_{\mathrm{equiv}}{}^{a}$/Å^2
Cr	0.5178(1)	0.3207(1)	0.5171(2)	3.33(5)
Cu	0.2475(1)	0.2561(1)	0.6787(1)	3.38(4)
O1	0.4482(4)	0.3423(3)	0.6434(7)	3.8(3)
O2	0.4416(4)	0.2572(3)	0.4902(7)	3.8(2)
O3	0.3393(4)	0.3143(3)	0.7061(7)	3.8(3)
O4	0.3360(5)	0.2231(3)	0.5546(8)	4.4(3)
O5	0.4389(4)	0.3589(3)	0.3625(8)	3.8(3)
O6	0.5747(5)	0.2848(3)	0.4062(7)	4.1(3)
O7	0.1749(4)	0.2971(3)	0.5268(8)	4.3(3)
N1	0.5949(6)	0.3852(4)	0.5747(9)	4.0(3)
N2	0.6159(5)	0.2932(4)	0.6848(9)	3.8(3)
N3	0.1685(5)	0.1949(4)	0.6464(9)	3.5(3)
N4	0.3054(5)	0.2391(4)	0.8806(9)	3.3(3)
C1	0.3913(6)	0.3085(4)	0.642(1)	3.0(3)
C2	0.3884(6)	0.2586(5)	0.555(1)	3.4(4)
C3	0.4441(7)	0.4055(4)	0.315(1)	3.4(4)
C4	0.3798(8)	0.4227(5)	0.193(1)	5.1(5)
C5	0.3837(9)	0.4718(6)	0.138(1)	6.2(5)
C6	0.453(1)	0.5066(6)	0.202(2)	7.4(6)
C7	0.5164(9)	0.4914(6)	0.323(1)	6.5(6)
C8	0.5146(8)	0.4415(5)	0.382(1)	4.5(5)
C9	0.5833(8)	0.4289(5)	0.510(1)	4.9(5)
C10	0.6705(7)	0.3798(5)	0.704(1)	4.7(4)
C11	0.6515(7)	0.3353(5)	0.785(1)	4.9(5)
C12	0.6572(7)	0.2498(5)	0.686(1)	4.5(4)
C13	0.6389(7)	0.2148(5)	0.568(1)	4.1(4)
C14	0.6684(8)	0.1631(5)	0.587(1)	5.1(5)
C15	0.6596(8)	0.1303(5)	0.478(2)	5.9(5)
C16	0.6200(8)	0.1503(5)	0.341(1)	5.2(5)
C17	0.5927(7)	0.2027(5)	0.319(1)	4.3(4)
C18	0.6001(6)	0.2359(4)	0.432(1)	3.7(4)
C19	0.0456(8)	0.3274(5)	0.360(1)	5.4(5)
C20	0.0929(7)	0.2846(5)	0.460(1)	3.9(4)
C21	0.497(7)	0.2402(4)	0.473(1)	3.5(4)
C22	0.875(7)	0.1967(5)	0.561(1)	3.6(4)
C23	0.0294(7)	0.1505(5)	0.554(1)	4.7(5)
C24	0.1970(7)	0.1472(5)	0.729(1)	4.0(4)
C25	0.2928(7)	0.1477(5)	0.810(1)	4.2(4)
C26	0.3192(6)	0.1885(5)	0.922(1)	3.7(4)
C27	0.3535(7)	0.1752(5)	1.063(1)	4.3(4)
C28	0.3745(8)	0.2161(5)	1.162(1)	4.9(4)
C29	0.3608(7)	0.2675(5)	1.118(1)	4.6(4)
C30	0.3259(7)	0.2776(5)	0.977(1)	3.5(4)
CD1	0.239(1)	−0.0712(6)	1.017(2)	8.8(7)
CD2	0.205(1)	−0.0637(7)	0.764(2)	9.6(8)
CD3	0.256(1)	0.0095(6)	0.913(2)	8.5(8)
ND1	0.2367(7)	−0.399(4)	0.902(1)	7.0(5)
OD1	0.2818(8)	0.358(5)	1.022(1)	10.1(5)
CD4	0.428(1)	0.102(1)	0.435(3)	18(1)
CD5	0.362(2)	0.0180(9)	0.387(3)	18(1)
CD6	0.335(2)	0.074(1)	0.537(3)	20(2)
ND2	0.3806(8)	0.0630(5)	0.460(1)	7.9(5)
OD2	0.289(1)	0.0425(8)	0.570(2)	21(1)
OM	0.5000(0)	0(0)	0(0)	21(3)
CM	0.5000(0)	0.034(1)	0.047(4)	10(2)

[a] Equivalent isotropic thermal parameters are calculated as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table II. Crystallographic Data for [Cr(salen)(ox)Cu(acpy)]2DMF·MeOH

formula	$C_{37}H_{47}N_6O_{10}CuCr$	V/Å^3	3986(3)
fw	851.36	Z	4
color	dark green	D_c/g cm^{-3}	1.419
cryst syst	monoclinic	D_m/g cm^{-3}	1.405
space group	$P2_1/n$	μ(Mo Kα)/cm^{-1}	8.60
a/Å	16.429(6)	dimens/mm^3	0.2 × 0.1 × 0.1
b/Å	25.303(14)	no. of reflcns	3327
c/Å	10.191(4)	R/%	7.86
β/deg	109.78(2)	R_w/%	7.09

Table III. Selected Bond Distances (Å) and Angles (deg) for [Cr(salen)(ox)Cu(acpy)]2DMF·MeOH

	Bond Distances (Å)		
Cr–O1	2.065(9)	Cr–O2	1.997(7)
Cr–O5	1.927(6)	Cr–O6	1.920(8)
Cr–N1	2.028(9)	Cr–N2	2.034(7)
Cu–O3	2.059(7)	Cu–O4	2.378(9)
Cu–O7	1.910(7)	Cu–N3	1.974(9)
Cu–N4	1.999(8)	Cr–Cu	5.482(3)
	Bond Angles (deg)		
O1–Cr–O2	81.1(3)	O1–Cr–O5	90.9(3)
O1–Cr–O6	167.1(3)	O1–Cr–N1	91.7(4)
O1–Cr–N2	90.8(4)	O2–Cr–O5	94.2(3)
O2–Cr–O6	87.0(3)	O2–Cr–N1	171.2(3)
O2–Cr–N2	97.0(3)	O5–Cr–O6	94.8(3)
O5–Cr–N1	90.8(3)	O5–Cr–N2	168.8(4)
O6–Cr–N1	99.8(4)	O6–Cr–N2	85.9(4)
N1–Cr–N2	78.0(4)	O3–Cu–O4	76.8(3)
O3–Cu–O7	87.0(3)	O3–Cu–N3	173.6(4)
O3–Cu–N4	86.7(3)	O4–Cu–O7	94.9(3)
O4–Cu–N3	97.1(4)	O4–Cu–N4	108.0(3)
O7–Cu–N3	95.5(3)	O7–Cu–N4	154.2(4)
N3–Cu–N4	93.5(4)		

The reaction of [Hpip][Cr(salen)(ox)] and [Cu(acpy)(H_2O)]ClO_4 formed complex **1** in a good yield. The reaction of stoichiometric amounts of [Hpip][Cr(salen)(ox)], a M(II) salt, and taea in an appropriate solvent and with $NaBPh_4$ added to the solution formed the complexes **2**–**5** as tetraphenylborate salts. Our attempts to obtain a Cr(III)–Cu(II) complex with taea were in vain. In the preparation of **1** heating or prolonging the reaction, even at room temperature, results in the precipitation of polymeric $\{Cu(ox)\}_n$. [Hpip][Cr(salen)(ox)] showed IR bands at 1680 cm^{-1} (ν(CO)) and 800 cm^{-1} (δ(CO)) which are typical of a nonbridging ox group. In **1**–**5** the corresponding IR bands were shifted to *ca.* 1660 and *ca.* 790 cm^{-1}, respectively, suggesting that the ox group acts as the bridge in each case. For **1** this is revealed by X-ray crystallography as described below.

Crystal Structure of 1′. The crystallographic data are presented in Table II and the relevant bond lengths and angles are presented in Table III. A view of the molecular entity with the atom-labeling scheme is presented in Figure 1.

The asymmetric unit cell contains one [Cr(salen)(ox)Cu(acpy)] molecule, two DMF molecules, and one MeOH molecule. The DMF and MeOH molecules are free from coordination and are captured in the lattice. The complex **1′** has an oxalate-bridged chromium(III)–copper(II) structure with a Cr···Cu distance of 5.482(3) Å. The chromium atom has a hexacoordinate *cis-β* configuration with the tetradentate salen in the folded form and a bidentate oxalate group. mhe Cr···O5 and Cr···O6 bond distances (1.927(6) and 1.920(8) Å, respectively) are shorter than the Cr···N1 and Cr···N2 bond distances (2.028(9) and 2.034(7) Å, respectively). One of the Cr–O(ox) bonds, Cr···O1 (2.065(9) Å), is significantly elongated compared to the other bond, Cr···O2 (1.997(7) Å). The coordination geometry around for the Cr(III) is essentially the same as that of [Hpip][Cr(salen)(ox)][7], except for the Cr···O1 bond length.

The geometry around the copper atom is regarded as a square-pyramid, where the basal coordination plane is defined by N3, N4, and O7 of the acpy ligand and O3 of the oxalate group. The deviations of the atoms from the least-squares plane are within 0.28 Å and the bond lengths in the basal plane fall within the range 1.910(7)–2.059(7) Å. The apical site O4 of the oxalate group is weakly coordinated with the Cu···O4 distance of 2.378(9) Å. This geometry is similar to that of ox-bridged dinuclear copper(II) complexes such as $[Cu_2(dien)_2(ox)]^{2+}$ (dien = diethylenetriamine), $[Cu_2(Me_5dien)_2(ox)]^{2+}$ (Me_5dien = 1,1,4,7,7-pentamethyldiethylenetriamine) and $[Cu_2(Et_5dien)_2(ox)]^{2+}$ (Et_5dien = 1,1,4,7,7-pentaethyldiethylenetriamine).[14–17]

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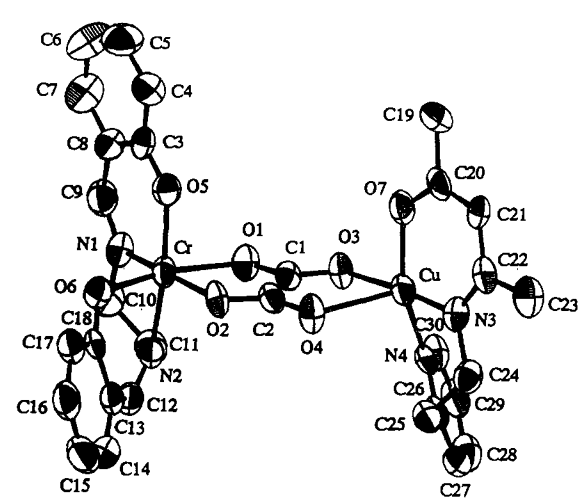

Figure 1. Molecular structure of [Cr(salen)(ox)Cu(acpy)]2DMF·MeOH with the atom-numbering scheme. Atoms are represented by their displacement ellipsolids at the 50% probability level.

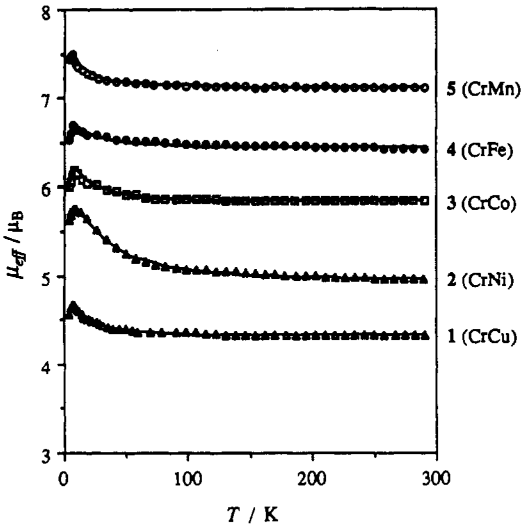

Figure 2. Plots of temperature-dependence of the effective magnetic moment μ_{eff} of **1**–**5**.

Magnetic Property. The cryomagnetic properties of **1**–**5** have been studied in the temperature range 4.2–300 K. The numerical data of the magnetic susceptibilities of **1**–**5** are given as supplementary data (Tables S1–S5). The μ_{eff} vs T plots of **1**–**5** are given in Figure 2, where μ_{eff} is the effective magnetic moment per CrM.

The effective magnetic moment of **1** is 4.32 μ_B at 290 K, which agrees with the spin-only value of 4.24 μ_B for Cr(III) ($S = {}^3/_2$)–Cu(II) ($S = {}^1/_2$) assuming no magnetic interaction. As the temperature is lowered, the magnetic moment increases gradually up to a maximum value of 4.66 μ_B at 6–8 K. The maximum value is close to the spin-only value of 4.90 μ_B for $S_T = 2$ resulting from the ferromagnetic coupling of $S_{Cr} = {}^3/_2$ and $S_{Cu} = {}^1/_2$. Thus, the observed magnetic behavior suggests an intramolecular ferromagnetic spin-exchange between the Cr(III) and Cu(II) ions through the oxalate bridge. A slight decrease in the magnetic moment below 6 K may be attributed to either an intermolecular antiferromagnetic interaction or a zero-field splitting of the Cr(III) ion. This effect is presumed to be a contribution from an intermolecular interaction and included in the parameter, θ, of our magnetic analyses. The magnetic susceptibility equation for the system, based on the isotropic spin Hamiltonian $\hat{H} = -2J\mathrm{S}_{Cr}\cdot\mathrm{S}_{Cu}$, is given by eq 1, where g_1 and g_2 are the g factors for the total spin-states $S_T = 1$ and 2, respectively, and the other

$$\chi_M = \frac{N\beta^2}{k(T-\Theta)} \times \frac{2g_1{}^2 + 10g_2{}^2 \exp(-4J/kT)}{3 + 5\exp(-4J/kT)} + N\alpha \quad (1)$$

symbols have their usual meanings. The g_1 and g_2 factors are associated with the g factors of the Cr(III) and Cu(II) ions and are expressed as $g_1 = {}^5/_4 g_{Cr} - {}^1/_4 g_{Cu}$ and $g_2 = {}^3/_4 g_{Cr} + {}^1/_4 g_{Cu}$, after the literature method.[18,19] The magnetic property of **1** can be well simulated by eq 1 using magnetic parameters $J = +2.8$ cm^{-1}, $g_{Cr} = 2.02$, $g_{Cu} = 2.09$, $\Theta = -0.5$ K, and $N\alpha = 160 \times 10^{-6}$ cm^3 mol^{-1}, as indicated by the solid line (trace **1**) in Figure 2. The discrepancy factor defined as $R(\mu) = [\sum(\mu_{obs} - \mu_{calc})^2/\sum\mu_{obs}{}^2]^{1/2}$ is 2.7×10^{-3}. Magnetic studies of **1′** were not made because this complex effloresced in the air.

The observed effective magnetic moment of **2** is 4.95 μ_B at 290 K, which is slightly larger than the spin-only value of 4.80 μ_B for Cr(III) ($S = {}^3/_2$)–Ni(II) ($S = 1$) without magnetic interaction. A gradual increase in the magnetic moment is observed as the temperature is decreased, indicating the presence of a ferromagnetic exchange interaction within the molecule. The maximum μ_{eff} value is 5.76 μ_B at 7.8 K which is very close to the spin-only value of 5.92 μ_B for $S_T = {}^5/_2$ resulting from the ferromagnetic coupling of $S_{Cr} = {}^3/_2$ and $S_{Ni} = 1$. Complex **2** shows a decrease similar to that of **1** in the magnetic moment at low temperatures. The magnetic analysis for **2** was carried out according to eq 2, which was derived from the isotropic spin

$$\chi_M = \frac{N\beta^2}{4k(T-\theta)} \times \frac{g_{1/2}{}^2 + 10g_{3/2}{}^2x^3 + 35g_{5/2}{}^2x^8}{1 + 2x^3 + 3x^8} + N\alpha \quad (2)$$

Hamiltonian $\hat{H} = -2J\mathrm{S}_{Cr}\cdot\mathrm{S}_{Ni}$, where $x = \exp(-J/kT)$ and the g factors of the total spin states $S_T = {}^1/_2, {}^3/_2$, and ${}^5/_2$ are given as follows: $g_{1/2} = {}^5/_3 g_{Cr} - {}^2/_3 g_{Ni}$, $g_{3/2} = {}^{11}/_{15} g_{Cr} + {}^4/_{15} g_{Ni}$ and $g_{5/2} = {}^3/_5 g_{Cr} + {}^2/_5 g_{Ni}$. A good magnetic simulation was obtained with eq 2 as indicated by the solid curve (trace **2**) in Figure 2, using magnetic parameters $J = +4.6$ cm^{-1}, $g_{Cr} = 2.03$, $g_{Ni} = 2.09$, $\Theta = -0.4$ K, and $N\alpha = 260 \times 10^{-6}$ cm^3 mol^{-1}. The $R(\mu)$ factor is 3.1×10^{-3}.

The effective magnetic moment of **3** is 5.85 μ_B at 290 K, which is larger than the spin-only value of 5.48 μ_B of the magnetically noninteracting Cr(III) ($S = {}^3/_2$)–Co(II) ($S = {}^3/_2$) system. As the temperature is lowered, the magnetic moment increases gradually and reaches a maximum value, 6.70 μ_B, at 6.3 K. This value is close to the spin-only value of 6.93 μ_B for $S_T = 3$ resulting from the ferromagnetic coupling of $S_{Cr} = {}^3/_2$ and $S_{Co} = {}^3/_2$. The octahedral cobalt(II) ion has the ground state ${}^4T_{1g}$, which should have a significant orbital contribution to the overall magnetic moment. In our magnetic analyses of **3**, the orbital contribution is included in the parameter g_{av} (average g factor), and the usual isotropic Heisenberg model is adopted. The magnetic susceptibility equation based on $\hat{H} = -2J\mathrm{S}_{Cr}\cdot\mathrm{S}_{Co}$ is given by eq 3, where

$$\chi_M = \frac{Ng_{av}{}^2\beta^2}{k(T-\Theta)} \times \frac{2x^2 + 10x^4 + 28x^{12}}{1 + 3x^2 + 5x^4 + 7x^{12}} + N\alpha \quad (3)$$

$x = \exp(-J/kT)$. A good magnetic simulation was obtained for **3** with eq 3 as indicated by trace **3** in Figure 2, using magnetic parameters $J = +1.3$ cm^{-1}, $g_{av} = 2.10$, $\Theta = -1.9$ K, and $N\alpha = 380 \times 10^{-6}$ cm^3 mol^{-1}. The $R(\mu)$ factor is 2.2×10^{-3}.

The effective magnetic moment of **4** is 6.42 μ_B at 290 K which is slightly larger than the spin-only value of 6.24 μ_B for Cr(III) ($S = {}^3/_2$)–Fe(II) ($S = {}^4/_2$), based on the assumption of no magnetic interaction. The magnetic moment increases gradually as the temperature decreases up to a maximum value of 6.70 μ_B at 6 K. The maximum value is smaller than the spin-only value of 7.94 μ_B for $S_T = {}^7/_2$ resulting from the ferromagnetic coupling

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Table IV. Summary of Exchange Integrals J for Oligomeric Cr(III)–ox–M(II) Complexes and J_{cal} for $\{NBu_4[MCr(ox)_3]\}_x$[a]

oligomeric Cr(III)–ox–M(II)			$\{NBu_4[MCr(ox)_3]\}_x$	
complex	J/cm^{-1}	ref		J_{cal}/cm^{-1}
1	+2.8	this work	M = Cu	+2.9
[Cr(salen)(ox)Cu(L^1)]	+2.2	21		
[Cr(salen)(ox)Cu(L^2)]	+2.7	21		
2	+4.6	this work	M = Ni	+3.6
$[Cr\{(ox)Ni(tetb)\}_3](ClO_4)_3$	+2.7	23		
$[Cr(OH)(H_2O)\{(ox)Ni(tetb)\}_2](ClO_4)$	+4.3	24		
3	+1.3	this work	M = Co	+1.9
4	+0.8	this work	M = Fe	+1.8
5	+0.5	this work	M = Mn	+0.7

[a] Abbreviations: L^1 = *N*-salicylidene-*N*-(2-pyridylethyl)aminate; L^2 = *N*-salicylidene-*N′*,*N′*-diethylenediaminate; tetb = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclodecane.

of $S_{Cr} = {}^3/_2$ and $S_{Fe} = {}^4/_2$, probably because of one of the following: an intermolecular antiferromagnetic interaction, a zero-field splitting of the Cr(III) and Fe(II) ions, or an orbital contribution of the $^5T_{2g}$ ground state of the octahedral Fe(II) ion. Magnetic analyses of **4** were carried out in the same way as that for **3** and the magnetic susceptibility equation for the system based on $\hat{H} = -2J\mathbf{S}_{Cr}\cdot\mathbf{S}_{Fe}$ is given by eq 4, where $x = \exp(-J/kT)$.

$$\chi_M = \frac{Ng_{av}^{\ 2}\beta^2}{4k(T-\Theta)} \times \frac{1 + 10x^3 + 35x^8 + 84x^{15}}{1 + 2x^3 + 3x^8 + 4x^{15}} + N\alpha \quad (4)$$

As indicated by trace **4** in Figure 2, a good magnetic simulation of **4** can be attained with this equation, using magnetic parameters $J = +0.8$ cm^{-1}, $g_{av} = 2.05$, $\Theta = -2.0$ K, and $N\alpha = 100 \times 10^{-6}$ cm^3 mol^{-1}. The $R(\mu)$ factor is 3.5×10^{-3}.

The effective magnetic moment of **5** at 290 K is 7.12 μ_B, which agrees well with the spin-only value 7.07 μ_B expected for Cr(III) ($S = {}^3/_2$)–Mn(II) ($S = {}^5/_2$) without any exchange interaction. In this complex, the plot of μ_{eff} vs T shows a gradual increase as the temperature decreases to 7.50 μ_B at 6 K, indicating a ferromagnetic exchange interaction between the Cr(III) and Mn(II) ions. The magnetic susceptibility expression for the Cr(III) ($S = {}^3/_2$)–Mn(II) ($S = {}^5/_2$) system based on the isotropic spin Hamiltonian $\boldsymbol{H} = -2J\mathbf{S}_{Cr}\cdot\mathbf{S}_{Mn}$ is given by eq 5, where $x =$

$$\chi_M = \frac{N\beta^2}{k(T-\Theta)} \times \frac{2g_1^{\ 2} + 10g_2^{\ 2}x^4 + 28g_3^{\ 2}x^{10} + 60g_4^{\ 2}x^{18}}{3 + 5x^4 + 7x^{10} + 9x^{18}} + N\alpha \quad (5)$$

$\exp(-J/kT)$. The g factors for the total spin-states from S_T = 1 to 4 are given as $g_1 = {}^7/_4 g_{Mn} - {}^3/_4 g_{Cr}$, $g_2 = {}^{11}/_{12} g_{Mn} + {}^1/_{12} g_{Cr}$, $g_3 = {}^{17}/_{24} g_{Mn} + {}^7/_{24} g_{Cr}$ and $g_4 = {}^5/_8 g_{Mn} + {}^3/_8 g_{Cr}$. A good least-squares fit of the data of **5** to eq 5 is achieved as shown by trace **5** in Figure 2, using the magnetic parameters $J = +0.5$ cm^{-1}, $g_{Cr} = 2.01$, $g_{Cu} = 2.00$, $\Theta = -1.3$ K, and $N\alpha = 100 \times 10^{-6}$ cm^3 mol^{-1}. The $R(\mu)$ factor is 2.4×10^{-3}.

The exchange integrals evaluated for **1**–**5** are summarized in Table IV. Thus, it appears that the magnetic interaction is ferromagnetic in all of the Cr(III)–ox–M(II) complexes.

In the simplest treatment of magnetic interaction in binuclear complexes only the SOMOs (singly occupied molecular orbitals) on the two magnetic centers are considered. The exchange interaction parameter $J_{MM'}$ is expressed by the mean of the individual interactions J_{ij} as eq 6, where n_i and n_j are the numbers

$$J_{MM'} = \frac{1}{n_i n_j}\sum_{i,j} J_{ij} \quad (6)$$

of unpaired electrons on metal ions M and M′. The copper(II) ion prefers an axially distorted configuration and has one unpaired electron on the $d_{x^2-y^2}$ orbital (x and y axes are taken along the donor atoms on the equatorial plane). In **1′** the equatorial plane is depicted by O3, O7, N3, and N4 so that the copper $d_{x^2-y^2}$ orbital interacts with the occupied MOs of the ox group with right symmetry, producing a magnetic orbital of σ-character. The chromium(III) ion prefers an octahedral (O_h) configuration and has three unpaired electrons on the t_{2g} (d_{xy}, d_{xz}, and d_{yz}) orbitals that interact with other occupied MOs of the ox group with right symmetry, producing magnetic orbitals of π-character. The overall exchange integral J_{CrCu} given by $(1/3)[J_{xy,x^2-y^2} + J_{xz,x^2-y^2} + J_{yz,x^2-y^2}]$ is positive because all the J_{ij} components are positive due to the orbital orthogonality of the magnetic orbitals.

The same argument is valid for **2**. The nickel(II) ion under O_h symmetry has two unpaired electrons on two σ-type magnetic orbitals formed with the $d_{x^2-y^2}$ and d_{z^2} of the Ni(II) ion. The J_{CrNi} given by $(1/6)[J_{xy,x^2-y^2} + J_{xz,x^2-y^2} + J_{yz,x^2-y^2} + J_{xy,z^2} + J_{xz,z^2} + J_{yz,z^2}]$ is again positive because all the J_{ij} components are positive due to orbital orthogonality. It should be noted that J_{CrNi} (+4.6 cm^{-1}) is larger than J_{CrCu} (+2.8 cm^{-1}). This fact suggests that the unpaired electron on the d_{z^2} orbital, compared with that on the $d_{x^2-y^2}$ orbital, has a large ferromagnetic interaction with the unpaired electrons of the Cr(III) ion, i.e., $(J_{xy,z^2} + J_{xz,z^2} + J_{yz,z^2}) > (J_{xy,x^2-y^2} + J_{xz,x^2-y^2} + J_{yz,x^2-y^2})$. On the basis of the first approximation that the $(J_{xy,x^2-y^2} + J_{xz,x^2-y^2} + J_{yz,x^2-y^2})$ value is the same ($3J_{CrCu} = +8.4$ cm^{-1}) for both **1** and **2**, the $(J_{xy,z^2} + J_{xz,z^2} + J_{yz,z^2})$ value is estimated to be +19.2 cm^{-1}.

In the case of **3**, **4**, and **5**, the M(II) ion (Co(II), Fe(II), and Mn(II), respectively) under O_h symmetry have unpaired electron(s) on the t_{2g} orbitals. The magnetic orbitals of the M(II) ion associated with the t_{2g} orbitals can overlap with the magnetic orbitals of the Cr(III) ion through the ox bridge, producing an antiferromagnetic contribution to the overall exchange integral. When we assume that the ferromagnetic contribution from the $(t_{2g})^3$(Cr)–$(e_g)^2$(M) interaction in these complexes is the same as that of **2** ($6J_{CrNi} = +27.6$ cm^{-1}), the antiferromagnetic contribution from the $(t_{2g})^3$(Cr)–$(t_{2g})^n$(M) coupling is estimated to be −15.9, −18.0, and −20.1 cm^{-1} for **3**, **4**, and **5**, respectively. Thus, in **3**–**5** the antiferromagnetic contribution is smaller than the ferromagnetic contribution. It also appears that the antiferromagnetic contribution tends to increase with the number of unpaired electrons on the M(II) t_{2g} orbital.

In a previous paper we reported that heterometal assemblies, $\{NBu_4[MCr(ox)_3]\}_x$, which are presumed to have a three-dimensional network structure extended through the Cr(III)–ox–M(II) linkage, show a ferromagnetic phase transition at T_c = 7 K for M = Cu, 14 K for Ni, 10 K for Co, 12 K for Fe, and 6 K for Mn.[6] It is of great value to examine the correlation between the phase-transition temperatures of $\{NBu_4[MCr(ox)_3]\}_x$ and the exchange integrals of the Cr(III)–ox–M(II) complexes **1**–**5**. According to Heisenberg's theory of ferromagnetism, the magnetic phase-transition temperature, T_c, of bimetallic three-dimensional ferromagnets can be approximated by eq 7,[20] where k denotes the Boltzmann constant, n is the number of the nearest

$$T_c = \frac{nJ_{\mathrm{cal}}}{3k}\sqrt{S_M(S_M + 1)S_{M'}(S_{M'} + 1)} \qquad (7)$$

M′ ions about the M ion (or vice versa), J_{cal} is the magnitude of the coupling constant between the nearest neighbors M–M′, and S_M and $S_{M'}$ are the spins of M and M′, respectively. The validity of eq 7, however, has not yet been proved experimentally.

On the basis of eq 7 ($n = 3$ in the present case) and using the phase-transition temperatures previously reported,[6,21] the coupling constants J_{cal} of the Cr(III)–ox–M(II) units of $\{NBu_4[MCr(ox)_3]\}_x$ are evaluated and are presented in Table IV. It must be emphasized that the J_{cal} values of $\{NBu_4[CuCr(ox)_3]\}_x$, $\{NBu_4[NiCr(ox)_3]\}_x$, $\{NBu_4[CoCr(ox)_3]\}_x$, $\{NBu_4[FeCr(ox)_3]\}_x$, and $\{NBu_4[MnCr(ox)_3]\}_x$ are in fair agreement with the J values of **1**–**5**, respectively. To the best of our knowledge, in addition to the present complexes, **1**–**5**, two Cr(III)–ox–Cu(II) and two Cr(III)–ox–Ni(II) complexes have also been reported so far. Oxalate-bridged dinuclear Cr(III)–Cu(II) complexes [Cr(salen)(ox)Cu(L^n)] (L^1 = *N*-salicylidene-*N*-(2-pyridylethyl)aminate; L^2 = *N*-salicylidene-*N′*,*N′*-diethylenediaminate) have been prepared in our laboratory,[21] and the spin-exchange integrals were estimated to be +2.2 and +2.7 cm^{-1}, respectively.[22] The exchange integrals of these complexes again agree well with the J_{cal} value (+2.9 cm^{-1}) of $\{NBu_4[CuCr(ox)_3]\}_x$. An oxalate-bridged tetranuclear Cr(III)–Ni(II) complex $[Cr\{(ox)Ni(tetb)\}_3](ClO_4)_3$[23] (tetb = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclodecane) was synthesized by Pei et al., and the J value between the Cr(III) and Ni(II) ions was estimated to be +2.7 cm^{-1}. Recently we prepared an oxalate-bridged trinuclear complex, $[Cr(OH)(H_2O)\{(ox)Ni(tetb)\}_2](ClO_4)$,[24] which shows a ferromagnetic spin-exchange interaction (J = +4.3 cm^{-1}) between the Cr(III) and Ni(II) ions. The J values for the Cr(III)–Ni(II) complexes were also close to the J_{cal} value (+3.6 cm^{-1}) of $\{NBu_4[NiCr(ox)_3]\}_x$. The exchange integrals of the previous ox-bridged complexes are also included in Table IV.

It should be noted that the geometry around the copper in **1′** is square-pyramidal, whereas the geometry about the copper in $\{NBu_4[CuCr(ox)_3]\}_x$ is supposed to be octahedral.[14–17] In **1′**, one ox oxygen occupies an equatorial site and the other oxygen occupies the axial site of the square-pyramidal copper, as commonly observed for five-coordinate oxalate–copper(II) complexes.[14–17] This type of bridge may leads to a reduced magnetic interaction between the Cr(III) and Cu(II) ions compared with the case where both ox oxygens occupy the equatorial sites of the copper(II) ion. It appears that the reduced magnetic interaction of **1** should be compared to the magnetic interaction between the nearest neighbors of $\{NBu_4[CuCr(ox)_3]\}_x$, because the octahedral copper(II) with the $(e_g)^1$ electronic configuration has a reduced spin-density on the magnetic orbital associated with its $d_{x^2-y^2}$ orbital. The good agreement between the J_{cal} value of $\{NBu_4[CuCr(ox)_3]\}_x$ and the J values of the Cr(III)–ox–Cu(II) complexes might be accidental, but the conformity between the J_{cal} and J values throughout the complexes given in Table IV is regarded as the first experimental evidence for the validity of eq 7.

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Supplementary Material Available: Tables giving bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations for **1′** and magnetic data for **1**–**5** (9 pages). Ordering information is given on any current masthead page. Structure factors are available upon request from the authors.

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