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# Multi-Dimensional Structures Constructed by the Electrostatic Interaction of Potassium Salts of Cobalt(III) and Manganese(III) Complexes with 1,2-Bis(2-hydroxybenzamido)benzene

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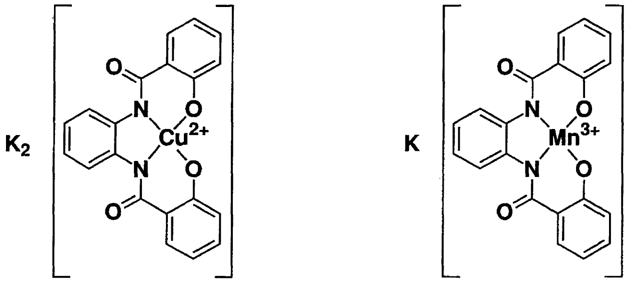
Potassium salts of cobalt(III) and manganese(III) complexes, $\mathrm{K[CoL(py)_2]\cdot 2EtOH\cdot MeOH}$ **1** and $\mathrm{K[MnL(py)_2]\cdot py}$ **2**, have been prepared, where $\mathrm{H_4L}$ = 1,2-bis(hydroxybenzamido)benzene and py = pyridine. **1** crystallizes in the monoclinic space group $P2_1/n$ with the cell dimensions of $a = 12.688(3)$, $b = 17.555(4)$, $c = 16.673(3)$ Å, $\beta = 102.59(2)°$, $V = 3624(1)$ Å$^3$, and $Z = 4$, in which potassium ion plays a role of connector for two adjacent $\mathrm{[CoL(py)_2]^-}$ molecules through K–O interaction (two phenoxo oxygen atoms of a cobalt(III) complex, two oxygen atoms of the solvent molecules, and an amido oxygen of the adjacent unit) to give an extended one-dimensional structure. **2** crystallizes in the orthorhombic space group $P2_12_12_1$ with the cell dimensions of $a = 14.358(1)$, $b = 16.457(2)$, $c = 13.703(2)$ Å, $V = 3237.7(5)$ Å$^3$, and $Z = 4$, in which potassium ion plays a role of connector for three adjacent $\mathrm{[MnL(py)_2]^-}$ molecules through K–O interaction to give an extended three-dimensional structure.

The fields of supramolecular chemistry and crystal engineering have attracted much attention, because the development of these fields is essential for creating new functional materials.[1,2] In order to produce supramolecular and extended multi-dimensional structures, a number of synthetic strategies, such as a metal-assisted self-assembly reaction,[3] a non-covalent interaction[4] via hydrogen bonds and/or a CH–π interaction, building-block methods,[5] and etc., have been proposed. Among them, a method using electrostatic cation–anion interaction would play an important role to build supramolecular[6] and extended multi-dimensional structures. In previous papers[7] we reported on the synthesis, structures, and properties of the potassium salts of nickel(II) and copper(II) complexes with 1,2-bis(2-hydroxybenzamido)ethane ($\mathrm{H_4L'}$) and with 1,2-bis(2-hydroxybenzamido)benzene ($\mathrm{H_4L}$). These complexes, with the general chemical formula of $\mathrm{K_2[Cu\ or\ Ni(L\ or\ L')]}$, are not only useful dianionic "ligand complexes" to produce a variety of heterometal polynuclear complexes, but also themselves have a unique one-dimensional crystal structure due to an electrostatic cation–anion interaction between the $\mathrm{K^+}$ ion and the dianionic metal complex, $\mathrm{[Cu\ or\ Ni(L\ or\ L')]^{2-}}$. In this work, we studied the cobalt(III) and manganese(III) complexes with the general formula of $\mathrm{K[Co\ or\ Mn(L)]}$ (see Scheme 1), and determined the crystal structures, since it can be expected that a monoanionic metal(III) complex $\mathrm{[Co\ or\ Mn(L)]^-}$ makes a different crystal structure with the $\mathrm{K^+}$ ion from that of a dianionic metal(II) complex. We report on a new one-dimensional structure of a cobalt(III) complex, $\mathrm{K[CoL(py)_2]\cdot EtOH\cdot MeOH}$ **1**, and a three-dimensional structure of a manganese(III) complex, $\mathrm{K[MnL(py)_2]\cdot py}$ **2**, constructed by electrostatic cation–anion interaction.



Scheme 1. Schematic structures of potassium *N*,*N'*-1,2-phenylenebis[2-carbamoyl-ϰ*N*-phenolato-ϰ*O*]cupurate(II) and -manganate(III).

## Experimental

**General Procedures and Materials.** All of the chemicals and solvents used for the synthesis were of reagent grade. The solvents used for physical measurements were purified by the methods described in the literature,[8] and stored under a nitrogen atmosphere. The quadridentate ligand, $\mathrm{H_4L}$, was prepared according to the literature.[9]

$\mathbf{K[CoL(py)_2]\cdot 2EtOH\cdot MeOH}$ **1.** Cobalt(II) acetate tetrahydrate, $\mathrm{H_4L}$, and potassium *t*-butoxide were mixed in methanol with a molar ratio of 1 : 1 : 4. The mixture was stirred for 2 h and then filtered. The filtrate was evaporated to dryness, and the residue was dissolved in a mixed solution of methanol and ethanol. To the solution was added a small amount of pyridine. The solution was then filtered. The filtrate was left stand in several days. During that time, brown crystals precipitated. Brown prisms. Anal. Calcd for $\mathrm{C_{35}H_{38}N_4O_7KCo}$: C, 58.95; H, 4.95; N, 8.09%. Found: C, 58.89; H, 5.02; N, 8.20%. IR/cm$^{-1}$ 1597 ($\nu_{\mathrm{CO}}$ (amido)). $\Lambda_{\mathrm{M}}$ 45 S cm$^2$ mol$^{-1}$ in DMF. U.V./nm (log $\varepsilon$) 507 (2.85) in DMF, 525 nm in solid state. $\mu_{\mathrm{eff}}$ (R.T.)/$\mu_{\mathrm{B}}$, diamag.

**K[MnL(py)$_2$]·py 2.** The complex was prepared by a method adapted for the cobalt(III) complex **1**, by using manganese(II) acetate tetrahydrate instead of cobalt(II) acetate tetrahydrate. Dark-brown prisms. Anal. Calcd for $C_{35}H_{27}N_5O_4KMn$: C, 61.65; H, 4.23; N, 10.12%. Found: C, 61.76; H, 4.15; N, 9.95%. IR/cm$^{-1}$ 1597 ($\nu_{CO}$ (amido)). $\Lambda_M$ 52 S cm$^2$ mol$^{-1}$ in DMF. U.V./nm (log $\varepsilon$) 488 (2.49) in DMF, 504 nm in solid state. $\mu_{eff}$ (R.T.)/$\mu_B$, 4.85.

**Physical Measurements.** Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Kyushu University. Electrical-conductivity measurements were carried out on a Horiba DS-14 conductivity meter in a $10^{-3}$ mol dm$^{-3}$ solution at room temperature. Infrared spectra were measured on KBr disks with JASCO A-102 spectrophotometers. Electronic spectra were measured on a Hitachi U-4000 spectrophotometer using $10^{-3}$ mol dm$^{-3}$ solutions. Magnetic susceptibilities were measured with a Faraday balance, where the calibration was made with [Ni(en)$_3$]$S_2O_3$ (en = ethylenediamine)$^{10)}$ and corrections were applied for diamagnetism calculated from Pascal's constants.$^{11)}$ The effective magnetic moments were calculated by the equation $\mu_{eff} = 2.828\,(\chi_A T)^{1/2}$, where $\chi_A$ is the magnetic susceptibility per formula unit.

**X-Ray Data Collection, Reduction, and Structure Determination.** All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda$ = 0.71069 Å) and a 12 kW rotating anode generator. The data were collected at a temperature of 20±1°C using the $\omega$–$2\theta$ scan technique at a scan speed of 16.0° min$^{-1}$ (in omega). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 3 scans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of the peak counting time to the background counting time was 2 : 1. The intensities of three representative reflections were measured after every 150 reflections, showing a good stability of the intensities. An empirical absorption correction based on azimuthal scans of several reflections was applied. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods$^{12)}$ and expanded using Fourier techniques.$^{13)}$ The non-hydrogn atoms were refined anisotropically. Hydrogen atoms were included in the structure-factor calculation. A full-matrix least-squares refinement based on the observed reflections ($I > 3.00\sigma(I)$) was employed, where the unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ are used. The weighting scheme was based on counting statistics. Neutral atomic scattering factors were taken from Cromer and Waber.$^{14)}$ Anomalous dispersion effects were included in Fcalcd; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.$^{14)}$ All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation.$^{15)}$

Crystal data and details of the structure determination are summarized in Table 1. Atomic coordinates for nonhydrogen atoms for K[CoL(py)$_2$]·2EtOH·MeOH **1** and K[MnL(py)$_2$]·py **2** are given in Tables 2 and 3, respectively. The atomic coordinates, thermal parameters, bond distances and angles, and $F_o - F_c$ tables were deposited as Document No. 71007 at the Office of the Editor of Bull. Chem. Soc. Jpn.

## Results and Discussion

**Synthesis and Characterization of K[CoL(py)$_2$]·2EtOH·MeOH 1 and K[MnL(py)$_2$]·py 2.** Complexes **1** and **2** were prepared by the reaction of metal(II) acetate tetrahydrate, $H_4L$, and potassium *t*-butoxide in methanol under an open atmosphere. Due to air oxidation, cobalt(III) and manganese(III) with tetraanionic quadridentate ligand, 1,2-bis(2-oxybenzamidato)benzene, were obtained as the potassium salts. Recrystallization of the complexes from a DMF solution involving a small amount of pyridine gave well-grown crystals suitable for X-ray analyses. The effective magnetic moment per metal is diamagnetic and 4.85 $\mu_B$ at room temperature for **1** and **2**, respectively. These data indicate that **1** assumes a low-spin state of Co(III) ion with $d^6$ and $S = 0$ and **2** assumes a high-spin state of Mn(III) ion with

Table 1. Crystallographic Data for K[CoL(py)$_2$]·2EtOH·MeOH **1** and K[MnL(py)$_2$]·py **2**

| Compound | **1** | **2** |
|---|---|---|
| Formula | $C_{35}H_{38}N_4O_7KCo$ | $C_{35}H_{27}N_5O_4KMn$ |
| Formula Weight | 724.73 | 675.66 |
| Crystal color | Brown | Dark brown |
| Crystal system | Monoclinic | Orthorhombic |
| Space group | $P2_1/n$ | $P2_12_12_1$ |
| $a$/Å | 12.688(3) | 14.358(1) |
| $b$/Å | 17.555(4) | 16.457(2) |
| $c$/Å | 16.673(3) | 13.703(2) |
| $\alpha$/deg | 90 | 90 |
| $\beta$/deg | 102.59(2) | 90 |
| $\gamma$/deg | 90 | 90 |
| $V$/Å$^3$ | 3624(1) | 3237.7(5) |
| $Z$ | 4 | 4 |
| $D_{cal}$/g cm$^{-3}$ | 1.328 | 1.386 |
| Radiation | Mo $K\alpha$ | Mo $K\alpha$ |
| $\mu$/cm$^{-1}$ | 6.39 | 5.82 |
| No. of reflections | 4751 | 2177 |
| $R$ | 4.6 | 6.3 |
| $R_w$ | 6.4 | 5.6 |

$R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = 1/[\sigma(F_o)^2]$.

Table 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen for K[CoL(py)$_2$]·2EtOH·MeOH **1**

| Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| Co1 | 0.17001(5) | 0.01482(3) | −0.21431(4) | 0.0302 |
| K1 | 0.2713(1) | 0.21344(7) | −0.16887(9) | 0.0584 |
| O1 | 0.3042(2) | 0.0663(2) | −0.2024(2) | 0.0351 |
| O2 | 0.1062(2) | 0.1125(2) | −0.2246(2) | 0.0369 |
| O3 | 0.3381(3) | −0.1694(2) | −0.2520(3) | 0.059 |
| O4 | −0.1414(3) | −0.0571(2) | −0.2824(3) | 0.052 |
| O5 | 0.4741(4) | 0.2568(3) | −0.0900(3) | 0.077 |
| O6 | 0.1614(4) | 0.1857(3) | 0.3762(3) | 0.070 |
| O7 | 0.1757(9) | 0.2840(7) | −0.0596(7) | 0.223 |
| N1 | 0.2350(3) | −0.0832(2) | −0.2026(2) | 0.034 |
| N2 | 0.0367(3) | −0.0387(2) | −0.2235(2) | 0.034 |
| N3 | 0.1569(3) | 0.0115(2) | −0.3334(2) | 0.035 |
| N4 | 0.1858(3) | 0.0220(2) | −0.0942(2) | 0.039 |
| C1 | 0.3908(4) | 0.0348(3) | −0.2212(3) | 0.033 |
| C2 | 0.4782(4) | 0.0841(3) | −0.2242(3) | 0.042 |
| C3 | 0.5702(4) | 0.0575(3) | −0.2455(4) | 0.048 |
| C4 | 0.5817(4) | −0.0188(3) | −0.2632(3) | 0.048 |
| C5 | 0.4982(4) | −0.0676(3) | −0.2589(3) | 0.044 |
| C6 | 0.4024(4) | −0.0429(3) | −0.2380(3) | 0.036 |
| C7 | 0.3219(4) | −0.1029(3) | −0.2317(3) | 0.038 |
| C8 | 0.1625(4) | −0.1390(3) | −0.1854(3) | 0.035 |
| C9 | 0.1931(4) | −0.2112(3) | −0.1537(3) | 0.046 |
| C10 | 0.1163(5) | −0.2598(3) | −0.1359(4) | 0.054 |
| C11 | 0.0091(5) | −0.2375(3) | −0.1488(4) | 0.052 |
| C12 | −0.0214(4) | −0.1655(3) | −0.1780(3) | 0.043 |
| C13 | 0.0548(4) | −0.1152(3) | −0.1969(3) | 0.036 |
| C14 | −0.0611(4) | −0.0140(3) | −0.2624(3) | 0.036 |
| C15 | −0.0760(4) | 0.0684(3) | −0.2820(3) | 0.035 |
| C16 | −0.1805(4) | 0.0909(3) | −0.3227(3) | 0.045 |
| C17 | −0.2064(4) | 0.1652(4) | −0.3430(4) | 0.057 |
| C18 | −0.1270(5) | 0.2208(3) | −0.3227(4) | 0.055 |
| C19 | −0.0244(4) | 0.2013(3) | −0.2837(3) | 0.046 |
| C20 | 0.0041(4) | 0.1252(3) | −0.2625(3) | 0.036 |
| C21 | 0.1791(4) | 0.0745(3) | −0.3719(3) | 0.044 |
| C22 | 0.1755(5) | 0.0768(4) | −0.4557(3) | 0.055 |
| C23 | 0.1499(5) | 0.0115(4) | −0.5013(3) | 0.062 |
| C24 | 0.1258(5) | −0.0540(4) | −0.4624(4) | 0.058 |
| C25 | 0.1292(4) | −0.0515(3) | −0.3785(3) | 0.044 |
| C26 | 0.2773(4) | 0.0007(3) | −0.0423(3) | 0.050 |
| C27 | 0.2908(5) | 0.0073(4) | 0.0413(4) | 0.067 |
| C28 | 0.2087(6) | 0.0359(5) | 0.0737(4) | 0.075 |
| C29 | 0.1147(6) | 0.0577(4) | 0.0209(4) | 0.073 |
| C30 | 0.1059(4) | 0.0498(4) | −0.0620(3) | 0.054 |
| C31 | 0.5047(9) | 0.2348(7) | −0.0067(6) | 0.124 |
| C32 | 0.491(1) | 0.1611(7) | 0.0120(7) | 0.171 |
| C33 | 0.2388(9) | 0.2302(6) | 0.3481(6) | 0.130 |
| C34 | 0.2784(9) | 0.2954(6) | 0.3953(7) | 0.130 |
| C35 | 0.083(1) | 0.279(2) | −0.0498(9) | 0.30 |

$B_{eq} = (8\pi^2/3)(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

Table 3. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen for K[MnL(py)$_2$]·py **2**

| Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| Mn | 0.2509(1) | 0.15201(10) | 0.0902(1) | 0.0459 |
| K | 0.4451(2) | 0.0735(1) | −0.0589(2) | 0.0480 |
| O1 | 0.3266(5) | 0.1954(4) | −0.0092(5) | 0.0490 |
| O2 | 0.3064(5) | 0.0498(4) | 0.0672(6) | 0.0546 |
| O3 | 0.1008(5) | 0.3565(5) | 0.0415(6) | 0.0656 |
| O4 | 0.1009(7) | 0.0136(5) | 0.2869(6) | 0.0827 |
| N1 | 0.1883(6) | 0.2548(5) | 0.1106(8) | 0.0502 |
| N2 | 0.1695(6) | 0.1116(6) | 0.1987(7) | 0.0434 |
| N3 | 0.1347(7) | 0.1129(6) | −0.0246(7) | 0.0550 |
| N4 | 0.3737(8) | 0.1799(7) | 0.2100(8) | 0.0588 |
| N5 | 0.5606(10) | −0.0561(8) | −0.0017(9) | 0.0725 |
| C1 | 0.3117(7) | 0.2647(7) | −0.0560(8) | 0.0427 |
| C2 | 0.3730(8) | 0.2846(7) | −0.1358(9) | 0.0533 |
| C3 | 0.3636(9) | 0.3549(8) | −0.1923(9) | 0.0581 |
| C4 | 0.2888(10) | 0.4052(8) | −0.1776(9) | 0.0690 |
| C5 | 0.2275(8) | 0.3859(7) | −0.0960(10) | 0.0672 |
| C6 | 0.2358(8) | 0.3172(6) | −0.0379(7) | 0.0417 |
| C7 | 0.1696(8) | 0.3109(7) | 0.0404(8) | 0.0459 |
| C8 | 0.1374(7) | 0.2537(7) | 0.2050(9) | 0.0446 |
| C9 | 0.1050(8) | 0.3246(8) | 0.2472(9) | 0.0560 |
| C10 | 0.061(1) | 0.3207(9) | 0.331(1) | 0.0707 |
| C11 | 0.0438(9) | 0.248(1) | 0.375(1) | 0.0850 |
| C12 | 0.0779(8) | 0.1754(8) | 0.3314(10) | 0.0621 |
| C13 | 0.1249(8) | 0.1776(8) | 0.2466(8) | 0.0430 |
| C14 | 0.1529(9) | 0.0337(7) | 0.2221(9) | 0.0493 |
| C15 | 0.1982(8) | −0.0316(7) | 0.1649(9) | 0.0486 |
| C16 | 0.1681(9) | −0.1109(8) | 0.1866(10) | 0.0628 |
| C17 | 0.203(1) | −0.1764(8) | 0.134(1) | 0.0750 |
| C18 | 0.2724(9) | −0.1667(8) | 0.058(1) | 0.0811 |
| C19 | 0.3025(8) | −0.0888(7) | 0.0380(10) | 0.0633 |
| C20 | 0.2690(7) | −0.0214(6) | 0.0903(9) | 0.0483 |
| C21 | 0.153(1) | 0.085(1) | −0.114(1) | 0.1034 |
| C22 | 0.090(1) | 0.055(1) | −0.188(1) | 0.1214 |
| C23 | −0.001(1) | 0.051(1) | −0.153(1) | 0.1075 |
| C24 | −0.0249(9) | 0.078(1) | −0.055(1) | 0.0860 |
| C25 | 0.045(1) | 0.1085(9) | 0.0001(8) | 0.0715 |
| C26 | 0.3658(9) | 0.1615(10) | 0.297(1) | 0.0787 |
| C27 | 0.439(1) | 0.167(1) | 0.367(1) | 0.1088 |
| C28 | 0.525(1) | 0.194(1) | 0.329(2) | 0.1119 |
| C29 | 0.533(1) | 0.213(1) | 0.239(1) | 0.1198 |
| C30 | 0.458(1) | 0.2053(9) | 0.184(1) | 0.0777 |
| C31 | 0.570(1) | −0.091(1) | 0.076(2) | 0.1055 |
| C32 | 0.650(2) | −0.128(1) | 0.115(2) | 0.1673 |
| C33 | 0.727(2) | −0.127(1) | 0.052(2) | 0.1357 |
| C34 | 0.713(2) | −0.094(1) | −0.024(2) | 0.1319 |
| C35 | 0.634(1) | −0.0590(10) | −0.052(1) | 0.0880 |

$B_{eq} = (8\pi^2/3)(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$.

$d^4$ and $S = 2$.

**Structural Description of K[CoL(py)$_2$]·2EtOH·MeOH 1.** An ORTEP view of the unique molecule of **1** with the atom numbering scheme is shown in Fig. 1. The one-dimensional structure running along the $b$-axis is shown in Fig. 2. Selected bond distances and interatomic distances between the K$^+$ and oxygen atoms are reported in Table 4. The cobalt(III) ion assumes an octahedral coordination geometry by two amido nitrogen and two phenoxo oxygen atoms of the quadridentate ligand and two nitrogen atoms of two pyridine molecules. The bond distances between the cobalt and the donor atoms of tetraanionic quadridentate ligand are 1.894 and 1.906 Å for the averaged values of ⟨Co–O⟩ and ⟨Co–N⟩, respectively. The bond distances of Co–N(pyridine) are

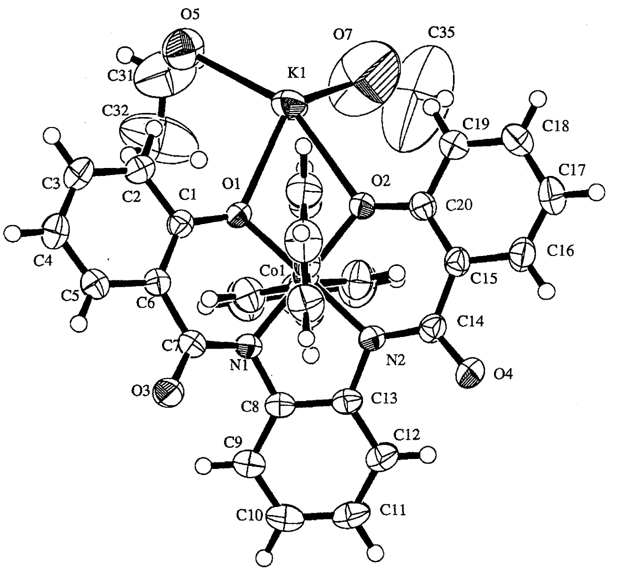


Fig. 1. An ORTEP drawing of $\mathrm{K[CoL(py)_2]\cdot 2EtOH\cdot MeOH}$ **1** with the atom numbering scheme, showing 50% probability ellipsoids.

Table 4. Relevant Bond Distances (Å) and Interatomic Distances (Å) around $\mathrm{K^+}$ with the Estimated Standard Deviations in Parentheses for $\mathrm{K[CoL(py)_2]\cdot 2EtOH\cdot MeOH}$ **1** and $\mathrm{K[MnL(py)_2]\cdot py}$ **2**

| | | | |
|---|---|---|---|
| (a) $\mathrm{K[CoL(py)_2]\cdot 2EtOH\cdot MeOH}$ **1** | | | |
| Co(1)–O(1) | 1.900(3) | Co(1)–O(2) | 1.888(3) |
| Co(1)–N(1) | 1.900(4) | Co(1)–N(2) | 1.912(4) |
| Co(1)–N(3) | 1.956(4) | Co(1)–N(4) | 1.972(4) |
| K(1)–O(1) | 2.695(3) | K(1)–O(2) | 2.746(3) |
| K(1)–O(3) | 2.664(4) | K(1)–O(5) | 2.731(5) |
| K(1)–O(7) | 2.699(9) | | |
| (b) $\mathrm{K[MnL(py)_2]\cdot py}$ **2** | | | |
| Mn–O(1) | 1.883(7) | Mn–O(2) | 1.888(7) |
| Mn–N(1) | 1.936(8) | Mn–N(2) | 2.005(9) |
| Mn–N(3) | 2.38(1) | Mn–N(4) | 2.45(1) |
| K–O(1) | 2.718(7) | K–O(2) | 2.665(8) |
| K–O(3) | 2.526(7) | K–O(4) | 2.639(8) |
| K–N(5) | 2.81(1) | | |

1.956(4) and 1.972(4) Å, which are slightly longer than those of Co-quadridentate ligand, indicating that the tetraanionic ligand supplies a strong ligand-filed. As shown in Fig. 2, the most striking feature of the crystal structure is an extended one-dimensional structure, in which a potassium ion playing the role of a connector is surrounded by two phenoxo oxygen atoms of a cobalt(III) complex $\mathrm{[CoL(py)_2]^-}$, two oxygen atoms of the solvent molecules (methanol and ethanol), and an amido oxygen atom of the adjacent cobalt(III) complex. The K–O distances are in the range of 2.664(4)—2.746(3) Å and the values are compatible with those for the potassium salt of the nickel(II) and copper(II) complexes reported

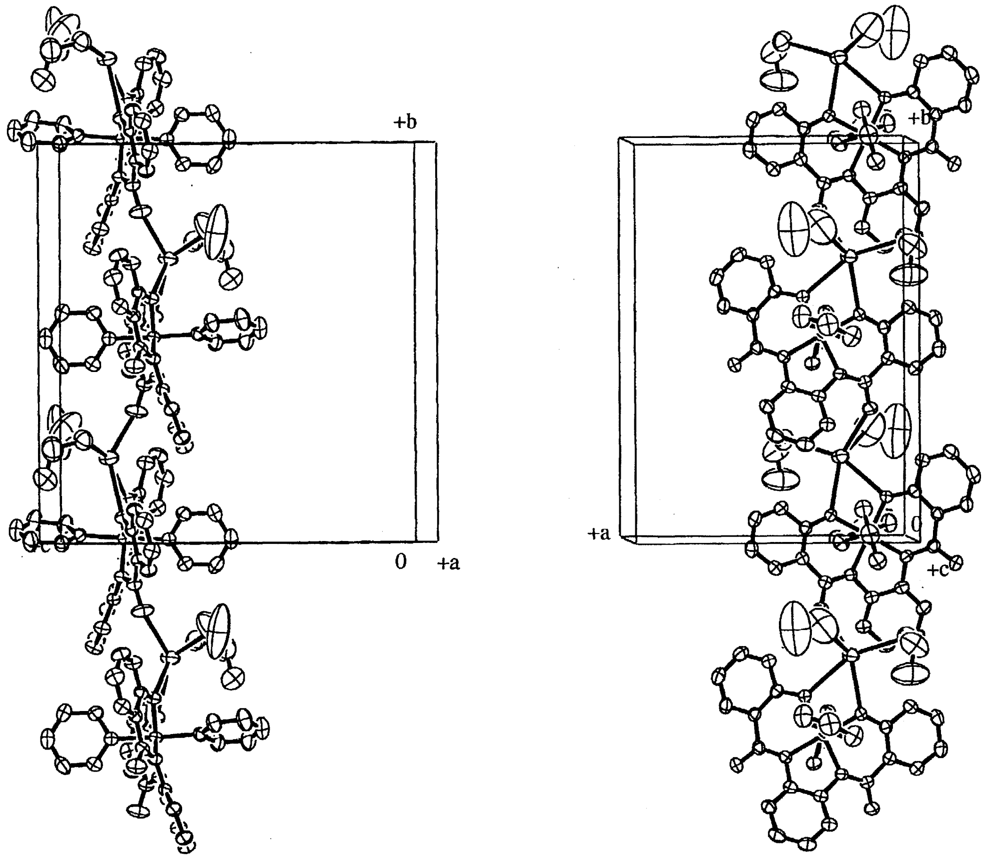
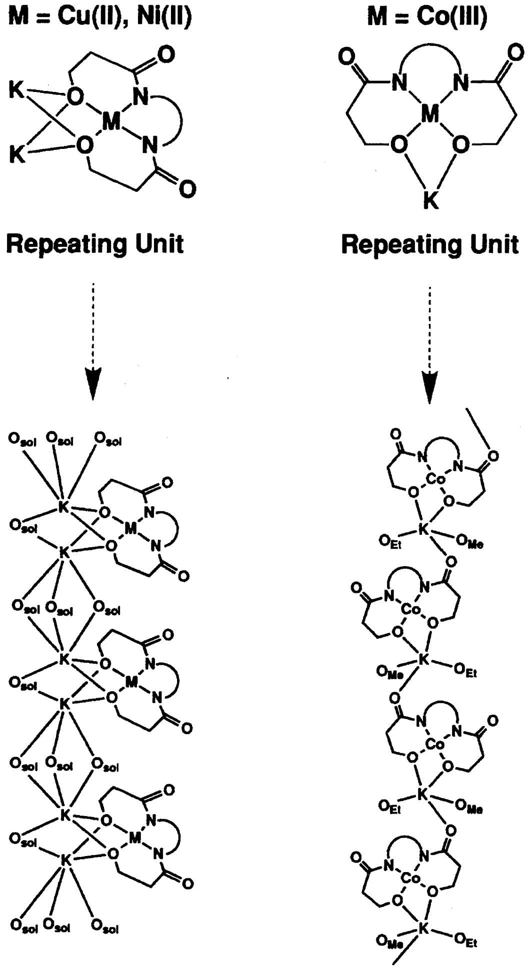


Fig. 2. (right) Projection along the *c*-axis of $\mathrm{K[CoL(py)_2]\cdot 2EtOH\cdot MeOH}$ **1**, showing a one-dimensional structure running along the *b*-axis. (left) Projection along the *a*-axis, showing an edge-on view of the one-dimensional structure.

previously and the potassium bis-crown ether compounds.[16] The potassium ion plays the role of a connector between the two adjacent $[\mathrm{CoL(py)_2}]^-$ ions through three K–O interactions, i.e., two K–O(phenoxo) interacitons of a cation and one K–O(amido) of an adjacent unit to give a one-dimensional structure consisting of $\{\mathrm{K(EtOH{\cdot}MeOH)CoL(py)_2}\}_n$ as the repeating unit.

The present one-dimensional structure is definitely different from the one-dimensional structure of $\mathrm{K_2[NiL']{\cdot}2DMF{\cdot}2H_2O}$ and $\mathrm{K_2[CuL]{\cdot}5DMF}$, whose structures are essentially the same as each other, in which $\mathrm{H_4L'}$ = 1,2-bis(2-hydroxybenzamido)ethane. These two kinds of one-dimensional structures are drawn schematically in Scheme 2. (1) In the former structure, each of the methanol and ethanol molecules as the crystal solvents interacts with one $\mathrm{K}^+$ ion by their oxygen atoms, while in the latter structures, each of DMF and water molecules interacts with two adjacent $\mathrm{K}^+$ ions, and their oxygen atoms function as bridging ligands for the adjacent two $\mathrm{K}^+$ ions. (2) In the former structure two phenoxo oxygen atoms of a monoanionic cobalt(III) complex interact with one $\mathrm{K}^+$ ion, while in the latter case two phenoxo oxygen atoms of a dianionic molecule interact with two $\mathrm{K}^+$ ions. (3) In the former structure one of the two amido oxygen atoms interacts with the $\mathrm{K}^+$ ion, and the resulting interaction participates in the construction of a one-dimensional structure, while in the latter case no amido oxygen atoms interact with the $\mathrm{K}^+$ ion. (4) In the former case, a planar monoanaionic molecule and a $\mathrm{K}^+$ ion array alternately roughly within a plane to give a planar tape-like structure as a repeating unit of $\{\mathrm{(K(solvents))(CoL(py)_2)}\}_n$; in the latter case, however, the planar dianaionic molecules array parallel to each other and perpendicular to the one-dimensional axis to form a cylindrical structure exhibiting a repeating unit of $\{\mathrm{K(solvents)K(NiL')}\}_n$.



Scheme 2. Schematic drawings of two kinds of one-dimensional structures for ($\mathrm{K_2[CuL]{\cdot}5DMF}$ and $\mathrm{K_2[NiL']{\cdot}2DMF{\cdot}2H_2O}$) and $\mathrm{K[CoL(py)_2]{\cdot}2EtOH{\cdot}MeOH}$ **1**, where amido oxygen does not participate in a formation of one-dimensional structure for the former compound but for the latter compound. The benzene rings are omitted for clarity.

**Structural Description of $\mathbf{K[MnL(py)_2]{\cdot}py}$ 2.** An ORTEP view of the unique molecule of **2** with the atom numbering scheme is shown in Fig. 3. Crystal packing diagrams showing an extended three-dimensional structure are given in Figs. 4 and 5. Selected bond distances and interatomic distances between $\mathrm{K}^+$ and oxygen atoms are reported in Table 4. It should be emphasized that the compound crystallizes in a noncentrosymmetric space group of $P2_12_12_1$. The manganese(III) ion assumes a square bipyramidal coordination geometry, where the equatorial coordination sites are occupied by two amido nitrogen and two phenoxo oxygen atoms of the quadridentate ligand with the average bond distances of ⟨Mn–O⟩ = 1.886 Å and ⟨Mn–N⟩ = 1.971 Å and the two axial coordination sites are occupied by two pyridine nitrogen atoms with distances of 2.38(1) and 2.45(1) Å. The bond distances of Mn–N (axially coordinated pyridine) are substantially elongated in comparison with those of the cobalt(III) complex **1**. The potassium ion is surrounded by

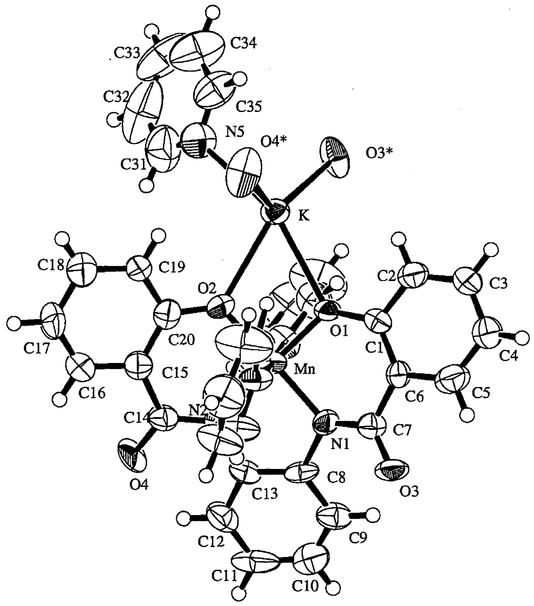


Fig. 3. An ORTEP drawing of $\mathrm{K[MnL(py)_2]{\cdot}py}$ **2** with the atom numbering scheme, showing 50% probability ellipsoids.

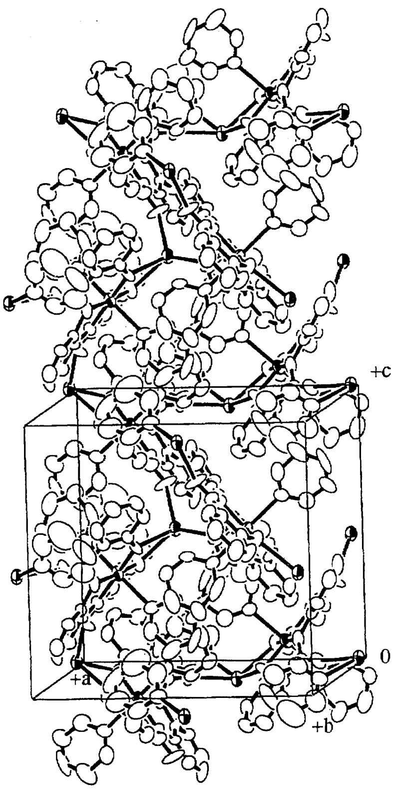


Fig. 4. Packing diagram of K[MnL(py)$_2$]·py **2**, showing a three-dimensional structure.

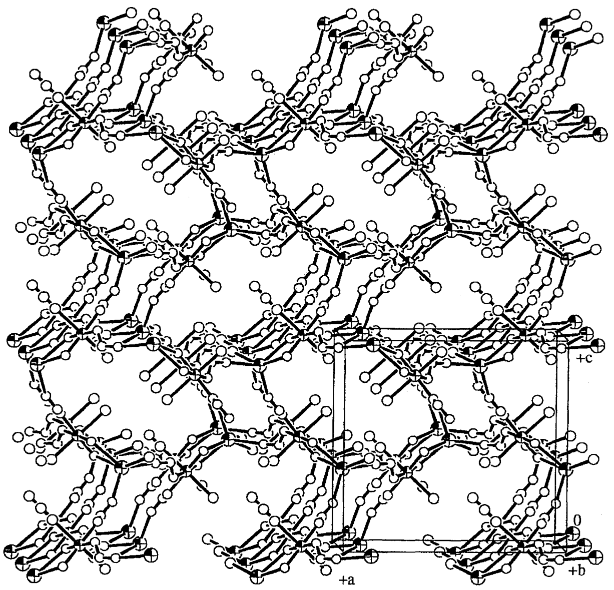
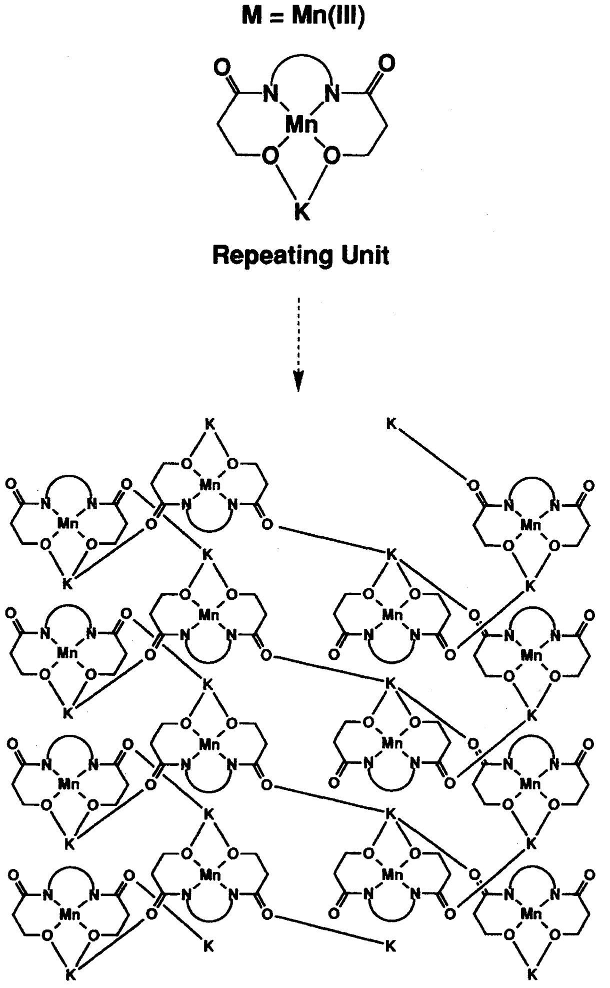


Fig. 5. Projection along the *b*-axis of K[MnL(py)$_2$]·py **2**, showing a three-dimensional structure. Only the atoms involved in the formation of an extended structure are drawn.

two phenoxo oxygen atoms of the first adjacent manganese(III) complex, an amido oxygen atom of the second adjacent Mn(III) molecule, an amido oxygen of the third adjacent molecule, and a nitrogen atom of pyridine molecule. The four K–O distances are in the range of 2.526(7)—2.718(7) Å and the values are compatible with those for the potassium salt of the nickel(II), copper(II), and cobalt(III) complexes and the potassium bis-crown ether compounds.[16] Since a potassium ion plays a role of connector for three neighboring Mn(III) molecules, a three-dimensional extended structure is constructed. A view projected along the *c*-axis (Fig. 4) shows how the K–O interactions produce the extended three-dimensional structure. Figure 5 demonstrates a channel structure and Scheme 3 shows the three-dimensional structure schematically. As can be seen in Scheme 3, a rod-like column structure is constructed by a helical linkage as a repeating unit involving two K$^+$ and two Mn molecules, and the adjacent columns are further connected by the interaction of K$^+$ and the remaining amido oxygen.

**Concluding Remarks.** The X-ray analyses of **1** and **2** as well as those of the nickel(II) and copper(II) complexes, reported previously, demonstrated that a variety of extended multi-dimensional structures can be constructed via an electrostatic cation–anion interaction. Floriani and coworkers[6] extensively studied the alkali metal ion adducts with *N*,*N*′- ethylenebis(salicylideneiminato)metal(II) and



Scheme 3. Schematic drawing of three-dimensional structure for K[MnL(py)$_2$]·py **2**, where two amido oxygen atoms as well as two phenoxo oxygen atoms per anionic molecule participate in a formation of the three-dimensional extended structure. The benzene rings are omitted for clarity.

-cobalt(I) (abbreviated as M(salen)) and reported the binuclear and oligonuclear structures. From the view point of constructing an extended structure, the present metal complexes with a tetraanionic quadridentate ligand involving both phenoxo and amido groups have many more advantages than the M(salen) system involving only phenoxo groups, because, in addition to the phenoxo group, an amido group can function as a ligand to an alkali metal ion, as demonstrated by the present work. Since the present result demonstrates that these anionic complex molecules are useful multidentate ligand-complexes, it is expected that not only oligonuclear compounds, but also extended multi-dimensional compounds exhibiting a magnetic phase transition, can be constructed by the reaction of these ligand complex and paramagnetic metal ions. If a paramagnetic metal ion instead of a potassium ion is substituted, the resulting multi-dimensional compound could be magnetic materials. A study along this line is now in progress in our laboratory.

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