# Formation of Metal-Oxygen Chain Structures by Bridging Dichromate and Coordination Compounds: $[ML_nCr_2O_7]_\infty$ ($ML_n$=$Cu^{2+}$(bipy), $Ni^{2+}(en)_2$, and $Ni^{2+}(bipy)_2$)

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Metal-oxygen linear chain compounds, $[Cu(bipy)Cr_2O_7]_\infty$ (**1**) (bipy = 2,2'-bipyridine), $[Ni(en)_2Cr_2O_7]_\infty$ (**2**) (en = ethylenediamine), and $[\{Ni(bipy)_2Cr_2O_7\}(CH_3CN)]_\infty$ (**3**) have been prepared and characterized. X-ray structural analyses of **1** to **3** revealed three chain structures: parallel in **1**, layers of chains which criss-cross in **2**, and helical in **3**. **1** to **3** form infinite chains through $-[Cr\text{-}O\text{-}Cr\text{-}O\text{-}M\text{-}O]_\infty-$ bonds. The conformations of oxygen atoms in $Cr_2O_7^{2-}$ are perfect eclipse in **1**, eclipse in **2**, and gauche-staggered conformation in **3** by means of the Neuman representation through Cr–Cr axis.

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Transition metal oxides have received increasing interest due to their diverse structures and properties.[1] Development of suitable model compounds is urgently required for better undertanding of the composite properties of the metal oxide.[2,3] One of the approaches to designing one-dimensional oxide polymers has been the synthesis by the combination of oxometalates and coordination compounds.[4] However, very few examples are known from which one-dimensional polymers are formed by utilizing polyoxometalate core as building blocks of the oxide polymer.[5] A recent example of an oxometalate bridged one-dimensional coordination polymers was provided by the work of Zubieta and his coworkers who used molybdate to form one- and two-dimensional organic-inorganic composite solids linked through $\{M(bipy)\}^{2+}$ fragments (M = Co, Ni, and Cu) by hydrothermal synthesis.[6,7] It is our aim to synthesize one-dimensional oxometalate bridged coordination complexes from metal oxo compounds and metal complexes having two coordination sites available for bridging. The structure of the chains may be controlled by varying the coordination environments of metal complexes used for bridging the oxometalate. The advantage of the use of dichromate over molybdate and tungstate as bridging ligands lies in the simplicity of solution equilibrium: i. e., in the case of molybdate and tungstate they tend to undergo complicated hydrolysis to give a variety of species, whereas only chromate and dichromate are involved in the equilibrium of dichromate. Here we report the syntheses and crystal structures of three dichromate bridged one-dimensional coordination polymers by using copper and nickel complexes.

The dichromate bridged complexes were obtained by reacting potassium dichromate with the corresponding compounds (**1**, $Cu(NO_3)_2$/bipy; **2**, $Ni(en)_2Cl_2$; **3**, $Ni(ClO_4)_2$/bipy). The resulting mixture yielded an orange yellow solution from which deep brown crystals of the composition $[ML_nCr_2O_7]_\infty$ (**1**: $ML_n$ = $Cu^{2+}$(bipy); **2**: $ML_n$ = $Ni^{2+}(en)_2$; **3**: $ML_n$ = $Ni^{2+}(bipy)_2$) were isolated[8] by slow evaporation of the solvent. In the case of compound **3**, further addition of organic solvent such as acetonitrile or acetone was necessary for crystallization. The complexes were hardly soluble in common organic solvents and water. The IR spectra of **1** to **3** show distinct bands due to ν(Cr=O) in the range of 800–900 $cm^{-1}$.

The X-ray structural analyses[9] revealed the infinite one dimensional chain structures with general formula $[ML_nCr_2O_7]_\infty$ constructed from coordination unit ($ML_n$) and dichromate ion which serves to bridge $ML_n$. The structures of oxide chains of **1** to **3** form infinite chains through $-[Cr\text{-}O\text{-}Cr\text{-}O\text{-}M\text{-}O]_\infty-$ bonds. The conformations of oxygen atoms in $Cr_2O_7^{2-}$ are perfect eclipse in **1**, eclipse in **2**, and gauche-staggered conformation in **3** by means of the Neuman representation through Cr–Cr axis.

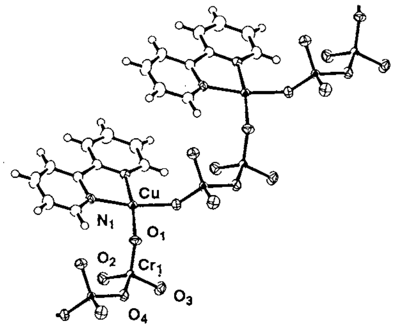

**Figure 1.** ORTEP drawing of **1**. Selected bond lengths (Å) and angles(°): Cu—$O_1$ = 1.958(2), $Cr_1$—$O_1$ = 1.647(2), $Cr_1$—$O_2$ = 1.781(1), Cu···Cu = 5.534(1), Cr···Cr = 3.226(1), Cu···$Cr_1$ = 3.680(1), $O_1$—Cu—$O_1$' = 91.5(1), $Cr_1$—$O_4$—$Cr_1$' = 129.8(1), $O_2$—$O_2$' = 3.002(4).

In compound **1**, bipyridine is coordinated to the distorted copper plane and the remaining *cis*-coordination sites are occupied by oxygen atoms of the dichromate bridging ligand (Figure 1). Thus, the resulting compound contains stair-like one-dimensional chains. The total propagation direction lies parallel to one another. The discrete analogue has been reported to lead to the formation of trinuclear complex, $[Cu(bipy)_2Cr_2O_7]$.[10]

Compound **2** consists of two independent nickel octahedron with bridging $Cr_2O_7^{2-}$ ion in an asymmetric unit (Figure 2a). The nickel center possesses the center of symmetry, and the equatorial coordination sites of the nickel ion are occupied by four nitrogen atoms of two symmetrically related ethylenediamines and axial sites are completed by two oxygen atoms of $Cr_2O_7^{2-}$ anion. The dihedral angle of the ethylenediamine planes defined by independent $NiN_4$ is 22.4°. The structure is similar to those of the corresponding copper complexes.[11] The relative orientation of chains has interesting features. The propagation direction of the chains lies parallel to one another consisting of layers of chains which form criss-crossed patterns within layer (Figure 2b). The chains cross one another at an angle of 28.1° from the Ni—Ni axis of the chains.

Compound **3** is characteristic in that the four nitrogen atoms of bipy occupying the nickel center form *cis*- coordination sites available for two bridging oxygen atoms of dichromate. The conformation of dichromate oxygens is gauche-staggered and the resulting infinite chains are helical (Figure 3). A pair of acetonitrile molecules are packed in the channel of the chains formed by bipy. It should be noted that a pair of acetones or *iso-*

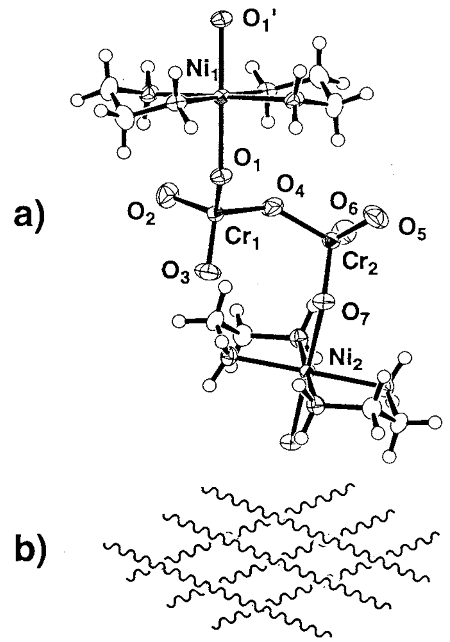

**Figure 2.** (a) ORTEP drawing of **2**. (b) A schematic packing diagram showing arrangement of chains into criss-crossed pattern along the crystallographic 001 direction. Selected bond lengths (Å) and angles(°): $Ni_1$—$O_1$ = 2.118(2), $Ni_2$—$O_7$ = 2.119(2), $Cr_1$—$O_1$ = 1.633(2), $Cr_2$—$O_7$ = 1.632(2), $Ni_1$···$Ni_2$ = 7.5570(9), $Cr_1$···$Cr_2$ = 5.8449(8), $Ni_1$···$Cr_1$ = 5.2577(6), $Cr_1$—$O_2$—$Cr_2$ = 139.6(2).

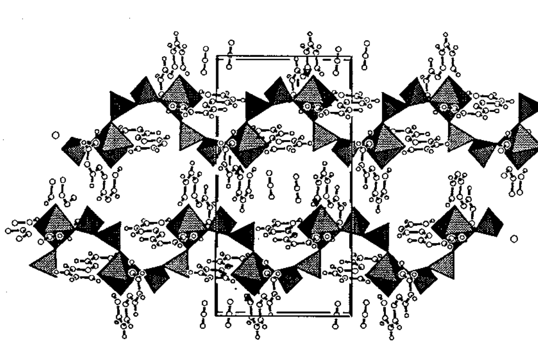

**Figure 3.** A view of the packing of **3** along the crystallographic 100 direction. The nickel $NiN_4O_2$ octahedra and chromium $CrO_4$ tetrahedra are represented by polyhedral representation. Selected bond lengths (Å) and angles(°): Ni—$O_1$ = 2.067(5), Ni—$O_5$ = 2.075(4), $Cr_1$—$O_1$ = 1.621(5), Ni···Ni = 7.747(1), $Cr_1$···$Cr_2$ = 3.246(2), $Ni_1$···$Cr_1$ = 3.577(1), $Ni_1$···$Cr_2$ = 3.539(1), $O_1$—Ni—$O_5$ = 88.1(2), $Cr_1$—$O_4$—$Cr_2$ = 132.8(3).

butyronitriles can be also packed in the channel to give isomorphous crystal.

We described the syntheses and structures of metal-oxygen linear chain compounds with bridging dichromate. The systematic variation of the linkage metal geometry where planar *cis*-, octahedral *trans*-, and octahedral *cis*- coordination sites are available for bridging dichromate leads to three linear chain structures. The environment of those metal centers affected by the dichromate conformation controls the chain structures. The chain structures of **1** to **3** arrange themselves in three motifs: parallel in **1**, layers of chains which criss-cross in **2**, and helical structure with inclusion of a pair of acetonitrile molecules within the chains in **3**.

## References and Notes

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8 The reaction was carried out by mixing the following chemicals. **1**, bipy:$Cu(NO_3)_2$:$K_2Cr_2O_7$ of 0.3:0.3:0.3 mmol in $H_2O$(20 $cm^3$)/Acetone(5 $cm^3$). Anal. Found: C, 27.66; H, 1.93; N, 6.51%. Calcd for $C_{10}H_8N_2O_7CuCr_2$: C, 27.57; H, 1.85; N, 6.43%.; **2**, $Ni(en)_2Cl_2$:$K_2Cr_2O_7$ of 0.5:0.5 mmol in $H_2O$(6 $cm^3$)/MeOH(1 $cm^3$). Anal. Found: C, 12.15; H, 4.09; N, 14.29%. Calcd for $C_4H_{16}N_4O_7NiCr_2$: C, 12.17; H, 4.08; N, 14.19%.; **3**, bipy: $Ni(ClO_4)_2$:$K_2Cr_2O_7$ of 0.3:0.3:0.3 mmol in $H_2O$(10 $cm^3$)/Acetone(3 $cm^3$). Anal. Found: C, 40.66; H, 2.79; N, 9.54%. Calcd for $C_{20}H_{16}N_4O_7NiCr_2$: C, 40.92; H, 2.75; N, 9.54%. Magnetic susceptibility data of **1** to **3** in the range of 7-300 K were well fit to the Curie-Weiss expression, indicating little coupling of paramagnetic centers.

9 Crystallographic data: $[Cu(bipy)Cr_2O_7]_\infty$ **1**: $M$ = 435.72, monoclinic, space group $C2/c$, $a$ = 7.679(1), $b$ = 20.087(2), $c$ = 8.754(1) Å, $\beta$ = 97.609(9)°, $V$ = 1338.4(2) $Å^3$, $Z$ = 4, $\mu$ = 32.1 $cm^{-1}$, 1696 total (1581 independent) reflections, $R_1$ = 0.024 for 1353 reflections, GOF = 1.3, $(\Delta/\sigma)_{max} < 0.10$, largest difference of peak and hole 0.34/-0.55 $e^-/Å^3$. $[Ni(en)_2Cr_2O_7]_\infty$ **2**: $M$ = 394.89, monoclinic, space group $C2/c$, $a$ = 29.419(4), $b$ = 6.945(2), $c$ = 13.107(2) Å, $\beta$ = 109.14(1)°, $V$ = 2530.1(8) $Å^3$, $Z$ = 8, $\mu$ = 31.9 $cm^{-1}$, 3211 total (3150 independent) reflections, $R_1$ = 0.026 for 2136 reflections, GOF = 1.19, $(\Delta/\sigma)_{max} < 0.01$, largest difference of peak and hole 0.29/-0.36 $e^-/Å^3$. $[\{Ni(bipy)_2Cr_2O_7\}(CH_3CN)]_\infty$ **3**: $M$ = 628.10, monoclinic, space group $P2_1/n$, $a$ = 9.251(4), $b$ = 11.961(4), $c$ = 22.681(3) Å, $\beta$ = 90.91(2)°, $V$ = 2509(1) $Å^3$, $Z$ = 2, $\mu$ = 16.4 $cm^{-1}$, 6419 total (6052 independent) reflections, $R_1$ = 0.044 for 2480 reflections, GOF = 1.25, $(\Delta/\sigma)_{max} < 0.10$, largest difference of peak and hole 0.37/-0.32 $e^-/Å^3$. All calculations were performed using teXsan Crystallographic Software package of Molecular Structure Corporation.

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